5-1-1969

Aerial Oxidation of Lith Developers

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AERIAL OXIDATION OF LITH DEVELOPERS

BY

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MAY 1969

An MS Program Research Thesis
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Accepted June 13, 1969

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ABSTRACT

Lith developers, unlike conventional developers, lose alkalinity when aerially oxidized. This is attributed to the alkaline reaction of the formaldehyde-bisulfite compound (FBS) commonly employed in lith developers as a "sulfite buffer". Conventional chemical analysis methods are used to obtain data and experimentally derive an equilibrium constant for the alkaline disassociation of FBS. Chemical and sensitometric data are presented that indicate that the alkalinity loss contributes significantly to the overall loss of developer activity. It is also shown that aeriating a lith developer quantitatively converts hydroquinone to hydroquinone monosulfonate that, in turn, is a measurably active developing agent. Additional data are presented that show that solution ionic strength strongly influences hydroquinone developer activity. This is attributed to increased ionization of hydroquinone. Finally, chemical analysis data are given that indicate that the accepted reaction for the aerial oxidation of conventional hydroquinone developers does not quantitatively apply when the sulfite concentration is in the range commonly employed in lith developers.

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1.0 Introduction

This work originated with the observation that lith developers lose alkalinity (decrease in pH) on undergoing aerial oxidation. Conversely, conventional photographic developers gain alkalinity (increase in pH) on undergoing aerial oxidation. Lith developers, when exposed to the atmosphere, lose activity considerably faster than conventional developers; therefore, it seemed reasonable that the observed alkalinity loss might be a significant factor in the overall loss of developer activity.

The initial goals of this project were:

(1) To establish that there is an inherent alkalinity loss in lith developers when they are aerially oxidized.

(2) To determine the contribution of this alkalinity loss to the overall loss of developer activity.

(3) To determine the major chemical reactions responsible for the loss in alkalinity.

As work on this project progressed, it became apparent that some of these initial goals and proposed test plans had to be revised. Revisions were necessitated primarily by the two following considerations:

(1) We originally assumed that only two changes would occur in aerially oxidizing a lith developer that would measurably contribute to its loss of activity. These changes were thought to be the loss of developing agent (through oxidation) and the previously observed decrease in solution alkalinity. We found, however, that when a lith developer is aerially oxidized the developer activity is additionally effected by an accompanying decrease in free sulfite and by the formation of hydroquinone monosulfonate. A scheduled 2-factorial experiment, designed to determine the contribution of alkalinity loss to the overall activity loss, was therefore inadequate and was replaced by experiments in which oxidized developer samples were restored to their initial levels of hydroquinone, pH and free sulfite and their photographic activity monitored before and after restoration.

(2) Closer consideration of the solution chemistry involved in lith developers led to the early realization that these developers indeed should lose alkalinity when aerially oxidized. This realization did not actually change the proposed test procedures. However, the third project goal was influenced in that we now understood that these developers should, in theory, lose alkalinity. The aim of the experiments then became to determine if the measured loss of alkalinity agreed with the theoretically predicted value. If not, we hoped to derive equations that would satisfactorily account for the experimental findings.

The most time consuming part of this project was the work aimed at determining the major chemical reactions responsible for the loss of lith developer alkalinity. We attempted to do this by subjecting simple lith developer formulations to a measured amount of aerial oxidation and measuring the change in concentration of the various components by chemical analysis performed before and after oxidation. The validity of some of the analytical procedures used is well established but some are certainly open to question, particularly regarding their application to systems in equilibrium. All of the analytical procedures used are consolidated in Section 8.0, even though some of them were developed as needed during the work. Included in this analytical procedures section are data obtained in attempting to establish the validity of a particular procedure and, in some cases, discussions relating the procedure to specific project applications.

Aside from the initial goals and scheduled work of this project, we found that solution ionic strength strongly influenced lith developer activity and considerable time was expended obtaining data establishing this fact and suggesting a probable explanation.

In attempting to order these different but inter-related topics in this thesis, it seems appropriate that we begin by establishing that alkalinity loss does occur in aerially oxidized lith developers and presenting a general explanation of the theoretical basis for this alkalinity loss. This, in turn, will serve as an introduction to the somewhat unique formaldehyde-bisulfite addition compound (FBS) used in these developers and to an early understanding of the importance of its reaction in alkaline solution. A good deal of the analytical chemistry involved in the project, as well as lith developer chemistry, is heavily dependent on the equilibrium reaction of formaldehyde bisulfite with alkali and on its remarkable resistance to oxidation in acid medium.

After the theoretical basis for alkalinity loss is discussed, the topics are presented in the order given in the table of contents. Each topic, in the usual case, will include an introduction and purpose of test, description of test procedures, test results and conclusions drawn from the data.

2.0 Establishing That a Lith Developer Does Lose Alkalinity on Undergoing Aerial Oxidation

2.1 Discussion: That an alkalinity loss does occur in an aerially oxidized lith developer is shown repeatedly in oxygen up-take and analysis runs documented later in this thesis. The following brief test is presented here simply to establish the fact that this occurs in commercial lith developers and to satisfy project goal #1 stated in the Introduction.

2.2 Test Plan: Carefully measure the pH of 1-liter of a commercial lith developer. Transfer the developer to a vacuum flask and slowly aeriate by means of an aspirator and fritted glass tube (assuring that the air used is CO_2 free by fitting a soda lime tube to the air inlet). Measure the pH of the developer after aeriating for various lengths of time.

2.3 Test Results:

	pH After Aeriating		
pH at Start	30 min	1 hour	2 hours
10.03	10.00	9.93	9.68

2.4 Conclusion: Commerical lith developers lose alkalinity (decrease in pH) when aerially oxidized.

3.0 Theoretical Basis for Alkalinity Loss in Autoxidized Lith Developers

Lith developers are uniquely formulated developers designed for use with lithographic films to yield images of extremely high contrast. Hydroquinone is employed as the sole developing agent. It is generally accepted that the active developing specie is actually a hydroquinone free radical, the semiquinone anion ($QH^{\cdot}$), that is generated in quantity during the development process by the mechanism:

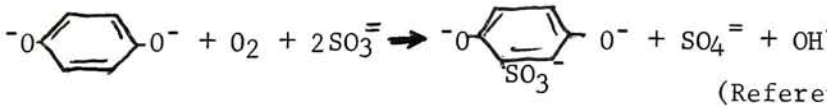
$$Q^{=} + Ag^{+} \longrightarrow Ag + QH^{\cdot}$$
$$QH^{\cdot} + Ag^{+} \longrightarrow Ag + Q$$
$$Q^{=} + Q \longrightarrow 2\ Q^{\cdot}$$

(Reference #1 and #2)

In order for lith development to take place, the developer must have a low free sulfite concentration. Lith developers are then essentially alkaline hydroquinone solutions containing sulfite at a sufficiently low level. This required low sulfite concentration can be obtained either by using a small quantity of a totally ionizing alkali sulfite (2 to 5 grams per liter as sodium sulfite) or by using a larger quantity of a sulfite "buffer" compound that partially disassociates in alkaline medium to yield the desired free sulfite concentration. All practical lith developers use the latter method. Sodium formaldehyde bisulfite is the sulfite "buffer" most commonly used.

If we aerially oxidize a conventional hydroquinone developer, or a lith developer in which the sulfite is entirely in the free state, the solution alkalinity increases according to the equation

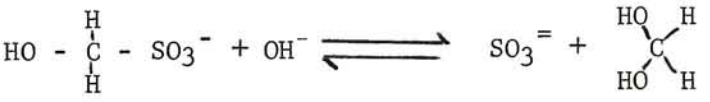
Eq 3.1



(Reference #14)

In this reaction, two moles of sulfite are consumed and one mole of hydroxide is generated to account for the observed increase in conventional developer alkalinity. If, however, sodium formaldehyde bisulfite (FBS) is the source of free sulfite for the developer, another chemical equation must also be considered. That is the equation by which free sulfite is generated by the reaction of FBS with alkali.

Eq 3.2

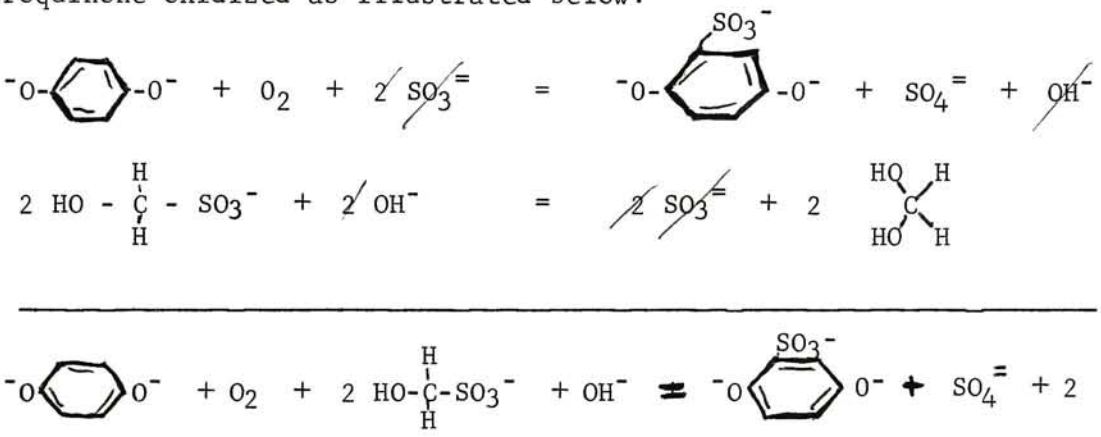


(Reference #3)

In this reaction, one mole of FBS reacts with one mole of hydroxide to form one mole of sulfite and one mole of hydrated formaldehyde. Observing again that Equation 3.1 consumes two moles of sulfite that in turn must be generated by Equation 3.2, we can simply double all components in Equation 3.2 and write:

Eq 3.3

If both Equation 3.1 and 3.2 were irreversable combining them would result in the overall loss of one mole or hydroxide for each mole of hydroquinone oxidized as illustrated below:

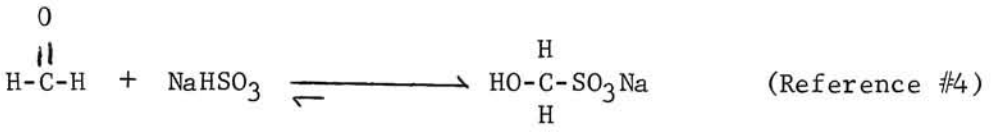


Equation 3.2 is, however, an equilibrium reaction.
If the concentration of one component is changed the equilibrium reaction will adjust itself according to the principal of Le Chatelier. For example, if sulfite is removed from the solution, the reaction will proceed to the right until equilibrium is once again established. At this new equilibrium condition, the FBS and hydroxide concentrations will be lower and the formaldehyde concentration higher than their concentrations at the initial equilibrium condition. Part, but not all, of the sulfite removed will be replaced as equilibrium is re-established. The exact proportion of the removed sulfite that will be replaced depends on the initial concentration of all four components and the specific equilibrium constant for the reaction. A good deal of data concerning this equilibrium equation is included in this work. But for the purpose of this generalized treatment, it is only necessary to state that with the component concentrations employed in lith developers, more than 50% of the sulfite lost by Equation 3.1 is replaced by sulfite generated by Equation 3.2. Noting again that Equation 3.1 consumes two moles of sulfite to generate one mole

of hydroxide, it is apparent that if precisely 50% of the sulfite lost by Equation 3.1 is replaced by sulfite generated by Equation 3.2 there would be no change in solution alkalinity. If more than 50% is replaced, there will be some loss of alkalinity and this is the condition existing in lith developers of this type.

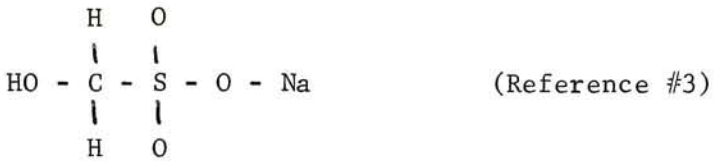
4.0 The Equilibrium Reaction of FBS with Alkali

Formaldehyde reacts rapidly with sodium bisulfite to form the formaldehyde bisulfite addition compound according to the equation



(Reference #4)

The addition compound has the structure of a sulfonic acid salt:



(Reference #3)

It is freely soluble in water, being fully ionized in aqueous solution, and exhibits other properties common to ionic salts (insoluble in either, infusible and nonvolatile). (Reference #4)

The FBS compound is remarkably stable in acid medium as very severe acidic oxidizing conditions are required to break the complex. On the other hand, FBS reacts readily with alkali to yield free formaldehyde and sulfite. It is this reaction that is of interest in connection with lith developers.

When considering the equilibrium reaction,

it seems that if we start with a known amount of FBS and determine the amount of free sulfite and formaldehyde present at a given pH, we could then calculate an equilibrium constant for the reaction. Without knowledge as to the approximate value of this constant, it is impossible to know how much FBS to use to obtain a given concentration of free sulfite or to determine if alkalinity changes are adequately explained in terms of the theory generalized in Section 3.0. This Section then deals largely with our efforts to determine this equilibrium constant in a simple lith developer and in alkaline FBS solutions.

Eastman (Practical Grade) FBS was used throughout this work. No attempt was made to further purify the compound. Several unsuccessful attempts were made to assay the FBS using acidic oxidizing methods. Conditions severe enough to break the complex (Ce^{++++} at near boiling temperatures) rapidly volatilized the formaldehyde and formic acid produced by the oxidation. An alkaline iodine analysis method (reference #5) gave replicate assay values of 101.4% and 103.0% as FBS. From this, it was decided that the purity of the compound was as good as any readily available means of assaying it; therefore, the practical grade FBS was used "as is" assuming it to be 100% FBS. We later determined that the FBS used in this work contained some free sulfite, ranging from 0.03% to 0.23% as $NaHSO_3$.

Experimental data are presented in this section much in the order that they were obtained in the laboratory work. First attempts at calculating an equilibrium constant used only pH and free sulfite determinations (assuming the initial free formaldehyde and free sulfite concentrations to be essentially equal). After a satisfactory free formaldehyde test was devised, equilibrium computations were made using pH, free sulfite and formaldehyde analysis data. Next, experiments were run in which free sulfite and then formaldehyde were added to lith developers and analyses made to determine if found values of free sulfite and formaldehyde agreed with values predicted for them from the previously computed equilibrium constant.

Next, the problem of restoring free sulfite in an oxidized lith developer to its original concentration is addressed. pH, sulfite and formaldehyde analyses are made on aeriated developers, the theoretical amount of sodium sulfite required to restore free sulfite to its original concentration is added, and analyses again performed. Additional data are given that indicate that solution ionic strength also influences the alkali-FBS equilibrium much as it does the alkali-hydroquinone equilibrium reaction discussed in Section 6.2.2.

Finally experiments are documented that involve acid/base titration of FBS and sodium sulfite in an effort to correlate free sulfite and formaldehyde analyses values with the amount of alkali consumed in generating them.

4.1 Determination of Free Sulfite and Equilibrium Calculations Based Only on Sulfite and pH Determinations

4.1.1 Replicate free sulfite determinations were run on a "Standard Unbuffered" lith developer prepared to be:

Hydroquinone	-	0.10 molar
FBS	-	0.50 molar
Potassium Bromide	-	0.017 molar

The pH was adjusted to the indicated value by adding 6.0 M NaOH. Replicate sulfite determinations were made at each pH level to get an estimate of the precision of the method. Results are tabulated in Table 4.1.1. Reproducibility is evidently quite good and since th "B" sample was run after "A" in each case, it seems that sulfite is being oxidized at a rate detectable between replicates.

TABLE 4.1.1

Sample	pH	Free Sulfite (as Na_2SO_3)
1A	9.65	1.06 g/1
1B	9.65	1.03 g/1
2A	9.81	1.31 g/1
2B	9.81	1.25 g/1
3A	10.00	1.61 g/1
3B	10.00	1.58 g/1
4A	10.19	1.95 g/1
4B	10.19	1.93 g/1

4.1.2 A test series totaling 12 free sulfite determinations was run on a 0.5 molar FBS solution, again with the pH adjusted to the indicated value with 6.0 M NaOH. Six samples (#1 - #6) were run one day and the other six the following day. The pH range covered in this series greatly exceeded the pH range over which a lith developer is operational.

Equilibrium calculations were then made based on the assumptions that:

$$(HCHO) = (Na_2SO_3)$$

$$(FBS) = (FBS)_{weighed} - (Na_2SO_3)$$

$$K = \frac{(HCHO)(Na_2SO_3)}{(FBS)(OH^-)} = \frac{(Na_2SO_3)^2}{(FBS)(OH^-)}$$

Table 4.1.2 gives the test results and the equilibrium constant calculated in each case. Results were fairly consistent except for Samples #1 and #7. Both of these were run on a 0.5 M FBS solution to which no NaOH had been added. A sizable error in the sulfite determination (a large relative error is likely at the low concentration) or pH measurement is probable.

TABLE 4.1.2

Sample #	pH	Na_2SO_3 (g/l)	Calculated Equilibrium Constant
1	5.76	0.047	49
2	8.28	0.234	3.65
3	9.50	0.908	3.30
4	9.79	1.24	3.18
5	10.00	1.67	3.57
6	10.20	1.94	3.09
7	5.52	0.056	120
8	9.08	0.579	3.54
9	9.64	1.08	3.42
10	9.92	1.38	2.96
11	10.51	2.78	3.19
12	11.00	4.79	3.13

If we disregard samples #1 and #7, to which no alkali was added, the values calculated for K have a standard deviation of 0.23 or a value for K of 3.30 ± 0.46 at a 95% confidence level.

4.2 Determination of Excess Sodium Bisulfite and of Free Sulfite and Formaldehyde with Corresponding Equilibrium Calculations

4.2.1 The assumption that (HCHO) = (Na_2SO_3) is only valid if the FBS is pure (contains no excess $NaHSO_3$) and then only at the initial equilibrium condition because, as oxidation takes place, the ratio of (HCHO)/(Na_2SO_3) changes. Therefore, it was necessary that a test be adapted for the independent determination of formaldehyde and that an estimation be made of the amount of excess Na HSO_3 present in the FBS.

Table 4.2.1 gives the % $NaHSO_3$ found by dissolving about 5 grams of FBS (accurately weighed) in acidified iodine and determining the equivalent amount of iodine consumed. (Essentially the same test as used for determining free sulfite.)

TABLE 4.2.1

FBS Sample	% $NaHSO_3$
EK Bottle #1	0.21%
EK Bottle #1 (replicate)	0.23%
EK Bottle #2	0.03%
Unmarked Can of FBS (obtained from Mr. T. Hill)	0.18%

These values for excess $NaHSO_3$ substantially agree with the initial differences found between (HCHO) and (Na_2SO_3) in subsequent solution analyses.

4.2.2 The determination for HCHO, described in the section on analytical methods, was devised and a test series was run on the Standard Unbuffered developer. Equilibrium calculations were made in which the only assumption is:

$$(FBS) = (FBS)_{weighed} - (HCHO)$$

Table 4.2.2 summarizes the results.

TABLE 4.2.2

Sample #	pH	$(Na_2SO_3)x10^{-2}$	$(HCHO)x10^{-2}$	K
1	9.61	0.825	0.680	2.80
2	9.90	1.13	0.880	2.56
3	10.20	1.60	1.32	2.75
4	9.73	0.882	0.787	2.63
5	10.07	1.29	1.18	2.66
6	10.21	1.51	1.37	2.63

This data yields an equilibrium constant of 2.67 $\pm$ .17 at a 95% confidence level. Unquestionably we cannot expect this kind of precision routinely as an error of only 0.02 in the pH determination will change K by about 0.15. A more representative collection of data might be taken from Table 4.4.2 in which we have seven cases of Na_2SO_3 and HCHO analyses that includes a fresh Standard Unbuffered developer and three samples each of the same developer after aeriation and restoration. The value of K calculated from this data is 3.02 $\pm$ .52 at a 95% confidence level.

$Na_2SO_3$and HCHO analyses performed on the Carbonate developer (Section 6.1.3) indicate an equilibrium constant for it of about 3.5. The somewhat higher value is attributed to the influence of solution ionic strength and is dealt with further in Sections 4.5 and 6.2.2.

Most of the data obtained in this project suggest an equilibrium constant of about 2.7 for the Standard Unbuffered developer and about 3.5 for the Carbonate developer.

4.3 Addition of Free Sulfite and Formaldehyde to a Standard Unbuffered Developer

4.3.1 Discussion: Adequate precision is indicated for the pH, $NaSO_3$ and HCHO determinations in the preceding tests. The accuracy of the methods were not necessarily demonstrated, however.

If the calculated constant is approximately correct, and if the Na_2SO_3 and HCHO determinations actually are measuring free sulfite and formaldehyde, we should be able to add known quantities of free Na_2SO_3 and free HCHO to the Standard Unbuffered developer and predict the new equilibrium concentration in each case. This is particularly important in the case of adding free sulfite because experiments are to be done in which it will be necessary to restore sulfite to its initial concentration.

Consider the Standard Unbuffered developer at equilibrium where

$$K = \frac{(Na_2SO_3)(HCHO)}{(FBS)(OH^-)} \simeq 2.7$$

or

$$(\text{Eq } \#4.3.1)\quad 2.7\ (FBS)(OH^-) \simeq (Na_2SO_3)(HCHO)$$

Addition of free sulfite or formaldehyde will result in some increase in FBS and OH^- concentrations. The amount of Na_2SO_3 or HCHO to be added however, will be quite small compared to the FBS concentration. Moreover, since the developer also contains hydroquinone, only a fraction of the OH^- generated will remain in the free state and be reflected as a change in pH. The increase in FBS concentration resulting from the small additions of formaldehyde and sulfite will also be small compared to the total FBS concentration. In Equation 4.3.1 then, the left side of the equation may, for practical purposes, be considered a constant $K^1 = 2.67$ $(OH^-)(FBS)$, where the concentrations are those present before addition of free sulfite or formaldehyde.

If we now add (m) moles per liter of sodium sulfite to a system in equilibrium, a portion of the added sulfite (x) will react and go to the complex and a portion will remain as free sulfite ((m)-(x)).

The new free sulfite and formaldehyde concentrations can then be defined as:

Eq #4.3.1.1 $(Na_2SO_3)_{new} = ((Na_2SO_3) + (m)-(x))$

Eq #4.3.1.2 $(HCHO)_{new} = ((HCHO)-(x))$

We now have the following approximation to the new equilibrium:

$$\underbrace{2.67\ (FBS)(OH)}_{\text{constant } K^1} = ((Na_2SO_3) + (m)-(x))\ ((HCHO)-(x))$$

Eq #4.3.1.3 $K^1 = (Na_2SO_3)(HCHO)+(HCHO)(m)-(Na_2SO_3)(x)-(m)(x)+(x)^2-(HCHO)(x)$

Noting that, by definition, $K^1 = (HCHO)(Na_2SO_3)$

Eq. #4.3.1.3 can be further reduced to:

Eq # 4.3.1.4 $(x)^2-(m)(x)-(Na_2SO_3)(x)-(HCHO)(x)+(m)(HCHO) = 0$

If we assume that the higher order $(x)^2$ term is negligible , we can eliminate it and Equation 4.3.1.4 reduces to:

$-(m)(x)-(Na_2SO_3)(x)-(HCHO)(x)+(m)(HCHO) = 0$

or

Eq #4.3.1.5 $$(x) = \frac{(m)(HCHO)}{(m)+(Na_2SO_3)+(HCHO)}$$

We now can estimate (x) through either quadratic equation 4.3.1.4 or equation 4.3.1.5. For a given m moles per liter sulfite added, we can then predict the new free sulfite concentration at equilibrium by simply substituting the values of (x) and (m) into equation #4.3.1.1. A similar set of equations, using the same approximations, can be developed for the addition of free formaldehyde.

It becomes apparent from the foregoing, however, that (m) and (x) are mutually dependent and in order to compute one, the other must be fixed.

This means that restoring sulfite to a preselected concentration is dependent both on (m) and (x). This problem will be treated later in Section 4.4. The immediately following test is intended only to determine if we can predict new equilibrium sulfite and formaldehyde concentrations by adding known amounts of reagent grade sodium sulfite and formaldehyde to a Standard Unbuffered developer.

4.3.2 Test Plan: A Standard Unbuffered lith developer was prepared and pH, free sulfite, and formaldehyde determinations made. Reagent grade sodium sulfite equivalent to 1.0, 2.0 and 3.0 grams per liter was added to the developer and new pH and free sulfite determinations were made. The same procedure was followed for reagent grade formaldehyde additions equivalent to 0.436, 0.680 and 0.934 grams per liter formaldehyde and subsequent determinations made for pH and formaldehyde. HCHO determinations were not made after Na_2SO_3 additions, and Na_2SO_3 determinations were not made after HCHO additions, except for the very last sample. This is done however in Section 4.4.

4.3.3 Test Results: Table 4.3.3.1 gives the analysis data obtained for the sulfite additions.

TABLE 4.3.3.1

Sample	pH	Na_2SO_3 (g/l)	HCHO (g/l)
Standard Unbuffered Developer	10.20	1.78	0.425
Standard Unbuffered + 1.0 g/l Na_2SO_3	10.21	2.32	not run
Standard Unbuffered + 2.0 g/l Na_2SO_3	10.21	3.28	not run
Standard Unbuffered + 3.0 g/l Na_2SO_3	10.23	4.02	not run

Table 4.3.3.2 gives the analysis data obtained for the free formaldehyde additions.

TABLE 4.3.3.2

Sample	pH	HCHO (g/l)	Na_2SO_3 (g/l)
Sample Unbuffered	10.21	0.405	1.76
Sample Unbuffered + .436 g/l HCHO	10.23	0.69	not run
Sample Unbuffered + .680 g/l HCHO	10.24	0.88	not run
Sample Unbuffered + .934 g/l HCHO	10.27	0.99	0.73

4.3.4 Computation of Predicted Sulfite and Formaldehyde Concentrations

Sulfite values were predicted by means of Equations 4.3.1.5 and 4.3.1.1.

Similar equations for the addition of formaldehyde are:

(m) = moles per liter added formaldehyde
(y) = moles per liter going to the complex

Eq #4.3.4.1 $$(y) = \frac{(Na_2SO_3)(m)}{(HCHO)+(m)+(Na_2SO_3)}$$

and

Equ #4.3.4.2 $$(HCHO)_{new} = (HCHO)_{old} + (m)-(y)$$

A sample calculation is given here as an example for a formaldehyde addition.

The Standard Unbuffered developer was analyzed for HCHO and Na_2SO_3. The (Na_2SO_3) was 1.76 g/l or 0.0140 molar and the (HCHO) was .405 g/l or 0.0135 molar. Free formaldehyde equivalent to 0.436 g/l or .0131 molar was added.

$$(y) = \frac{(0.0140)(0.0131)}{(0.0135)+(.0131)+(0.0140)} = \frac{18.35 \times 10^{-5}}{4.06 \times 10^{-2}} = .0045 \text{ molar}$$

then

$$(HCHO)_{new} = 0.0135 + 0.0131 - 0.0045 = 0.0221 \text{ molar}$$

This equivalent to 0.66 grams per liter formaldehyde as compared to the 0.69 g/l found (Row 2, Table 4.3.3.2).

Table 4.3.4.1 lists the predicted (calculated) Na_2SO_3 and HCHO concentrations and the values found by analyses.

TABLE 4.3.4.1

Grams/Liter Na_2SO_3 Added	Grams/Liter HCHO Added	Grams/Liter Found	Grams/Liter Predicted
1.0	-	2.32	2.39
2.0	-	3.28	3.14
3.0	-	4.02	4.02
-	0.436	0.69	0.66
-	0.680	0.88	0.92
-	0.934	0.99	1.08

These results seem to indicate that:

(1) The Na_2SO_3 and HCHO determinations are measuring free Na_2SO_3 and free HCHO with reasonable accuracy.

(2) The approximations used in deriving the prediction equations are valid for the range of HCHO and Na_2SO_3 additions employed.

(3) The HCHO determination tends to give low results at higher HCHO concentrations.

4.4 Restoring Free Sulfite to its Initial Concentration in an Oxidized Lith Developer

When a lith developer is aerially oxidized free sulfite is removed from the solution by the formation of HQS and sulfate. Some of the removed sulfite is replaced by the alkaline disassociation of FBS as discussed in Section 3.0. We are faced with the problem, however, of how much sodium sulfite to add to such an oxidized developer to restore it to its initial free sulfite concentration. This problem is associated with attempts to measure the contribution of various components to decreased photographic activity as documented in Section 6.2.3 and 6.1.3. We have considered the problem from the viewpoint of restoring the developer free sulfite at its initial pH and not of restoring sulfite at the lower pH of the oxidized developer. This approach removes any dependence on the value of the equilibrium constant.

Consider the case where (m) moles per liter of sulfite are removed by oxidation to form HQS and sulfate. Let (x) be the moles per liter sulfite replaced by the alkaline disassociation of FBS. Then

Eq #4.4.0.1 $$(Na_2SO_3)_{oxidized} = (Na_2SO_3)_{initial} + (x) - (m)$$

and

Eq #4.4.0.2 $$(HCHO)_{oxidized} = (HCHO)_{initial} + (x)$$

To restore the sulfite we simply need to determine the amount removed (m) by oxidation and add this back to the developer as Na_2SO_3. If we analytically determine the free sulfite and formaldehyde concentrations in the initial and oxidized developer, we can first compute (x) directly from the HCHO analyses and then use this value to compute (m) from the sulfite analyses. The necessary forms of the equations are:

Eq #4.4.0.3 $$(x) = (HCHO)_{oxidized} - (HCHO)_{initial}$$

Eq #4.4.0.4 $$(m) = (Na_2SO_3)_{initial} + (x) - (Na_2SO_3)_{oxidized}$$

This treatment is not dependent on any particular value of the equilibrium constant and the only assumption is that formaldehyde is not removed from the solution once it is free of the FBS complex.

The following test series was performed to see if we can accurately restore the free sulfite concentration in oxidized developers using free sulfite and formaldehyde analysis data.

4.4.1 Test Plan:

(1) Prepare 2-liters of the Standard Unbuffered developer adjusting the pH to about 10.20.

(2) Determine the initial pH, (Na_2SO_3) and (HCHO).

(3) Aeriate until a pH change of about 0.1 to 0.2 is indicated.

(4) Determine pH, (Na_2SO_3) and (HCHO) in the aeriated developer.

(5) Compute the amount of Na_2SO_3 to be added to 500 ml of the developer.

(6) Add the calculated amount of Na_2SO_3 to a 500 ml aliquot of the developer and adjust to the initial developer pH. Determine (Na_2SO_3) and (HCHO).

(7) Continue aeriating the remaining developer and repeat steps 3 through 6 on two more 500 ml samples at decreasing pH values.

4.4.2 Test Results: The results of the analyses and the amounts of Na_2SO_3 added are given in Table 4.4.2.

TABLE 4.4.2

	pH	(Na_2SO_3)	(HCHO)	Na_2SO_3 Added (grams/500 ml)
(1) Initial Developer	10.21	0.0166	0.0146	-
(2) 1st Aeriation	10.06	0.0060	0.0289	-
(3) 1st Na_2SO_3 Restoration	10.21	0.0169	0.0154	1.57
(4) 2nd Aeriation	9.95	0.0031	0.0361	-
(5) 2nd Na_2SO_3 Restoration	10.21	0.0173	0.0134	2.26
(6) 3rd Aeriation	9.77	0.0018	0.0450	-
(7) 3rd Na_2SO_3 Restoration	10.21	0.0174	0.0128	2.84

4.4.3 Conclusion: The initial free sulfite concentration was 2.09 g/l as Na_2SO_3. The free sulfite in the three restored samples was 2.13, 2.18 and 2.19 g/l respectively. All restored samples were then within 5% of the initial free sulfite concentration. This method therefore seems adequate for restoring free sulfite in oxidized lith developers and was used to do so on one Standard Unbuffered and three Carbonate developers in Sections 6.1.2 and 6.1.3. The free sulfite concentration after restoring was checked only on the Standard Unbuffered developer and on Carbonate developer #1. In these cases the free sulfite was determined after the developers had been "fully" restored and sensitometric strips processed. The Standard Unbuffered developer was 1.80 g/l initially compared to 1.92 g/l restored and the Carbonate developer was 2.44 g/l initially compared to 2.14 g/l restored. Any difference in photographic activity due to these differences in free sulfite concentration would be very small and that is the total objective of restoring free sulfite in this project.

The data in Table 4.4.2 seems to indicate a trend in that successive restorations result in progressively higher (Na_2SO_3) and lower (HCHO) values. Generally speaking, however, I am pleased and somewhat surprised at the good agreement found between theory and analysis results. This adds considerably to the validity of the free sulfite and formaldehyde determinations employed.

Table 4.4.3 gives the values of (m) and (x) computed and shows the ratio of (x) to (m). This ratio, in theory, is the fraction of sulfite removed that is replaced by alkaline disassociation of the FBS complex.

TABLE 4.4.3

Solution	(x)	(m)	$\frac{(x)}{(m)}$
1st Aeriation	0.0143	0.0248	0.58
2nd Aeriation	0.0215	0.0359	0.60
3rd Aeriation	0.0304	0.0452	0.67

This indicates that as oxidation proceeds, a greater proportion of the removed sulfite is replaced by disassociation of FBS. This in turn means that alkalinity loss would be accelerated as the free sulfite concentration decreases.

As stated previously, this method of restoring free sulfite requires no knowledge of the alkali-FBS equilibrium constant and is applicable to any lith developer so long as we determine (HCHO) and (Na_2SO_3) initially and at the current state of oxidation. If we want to restore free sulfite to its initial concentration and adjust the pH to any value other than its original value, we must know the approximate value of the equilibrium constant.

4.5 The Influence of Solution Ionic Strength on the Alkali-FBS Equilibrium

4.5.1 Discussion: The Debye-Huckel theory (refer to Section 6.2.2) predicts that increasing solution ionic strength would increase the reaction rate between $HOCH_2SO_3^-$ and OH^- and would therefore increase the concentration of HCHO and Na_2SO_3 at a given pH. That is, the value of the equilibrium constant K where

$$K = \frac{(SO_3^=)(HCHO)}{(HOCH_2SO_3^-)(OH^-)}$$

would increase with increasing solution ionic strength. The following test was run to determine if this is true.

4.5.2 Test Plan:

(1) Prepare one liter of 1.5 molar FBS.

(2) To one 500 ml portion (A), add 500 ml of distilled water. To the remaining 500 ml portion (B), add 500 ml of 1.5 molar Na_2SO_4.

(3) The ionic strengths of the two solutions are:

A = 0.75 molar B = 3.0 molar

(4) Add 6.0 N NaOH to each, record the pH and analyze for Na_2SO_3 and HCHO.

(5) Repeat step 4 two more times for each solution.

(6) From the pH value, (Na_2SO_3) and (HCHO) compute the alkali-FBS equilibrium constant.

4.5.3 Test Results: Table 4.5.3 shows the analysis results obtained and the equilibrium constant computed for each set of data.

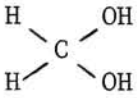
TABLE 4.5.3

SOLUTION A (u = .75 molar)				SOLUTION B (u = 3.0 molar)			
pH	9.89	10.23	10.50	pH	9.82	10.19	10.53
(HCHO)	0.0135	0.0196	0.0280	(HCHO)	.0175	0.0257	.0388
(Na_2SO_3)	0.0157	0.0229	0.0319	(Na_2SO_3)	.0198	0.0292	.0422
K	3.7	3.6	3.9	K	7.2	6.7	6.8

4.5.4 Conclusion: The average of the three equilibrium constants for the 0.75 molar ionic strength solution is 3.7 compared to an average value of 6.9 for the 3.0 molar ionic strength solution. Evidently increasing ionic strength does accelerate the reaction between FBS and alkali as predicted by the Debye-Huckel theory. The magnitude of the influence is certainly sufficient to warrant consideration in practical formulation of lith developers.

4.6 Alkaline Titration of FBS

4.6.1 Discussion:

Eq 3.2 $HOCH_2SO_3^- + OH^- \rightleftharpoons SO_3^= +$ 

The above equation states that every hydroxide ion consumed in reacting with FBS will generate an equivalent amount of sulfite and formaldehyde. If we add a known amount of hydroxide to an aqueous FBS solution, a portion of the added OH^- reacts with the complex and a portion remains as free OH^-. If we can determine the amount remaining as free OH^-, by the solution pH or by other means, we can subtract this from the OH^- added and get the amount consumed. This in turn should be equivalent to our analyses values for sulfite and formaldehyde generated.

The following alkaline titrations and sulfite and formaldehyde analyses were done with this in mind.

4.6.2 Test Plan:

(1) Potentiometrically titrate 200 ml of 0.10 M FBS and then 200 ml of distilled H_2O with 1.00 N NaOH. Plot the titration curves.

(2) To 3 separate 200 ml portions of 0.10 M FBS add a known volume of 1.00 N NaOH, record the pH then determine Na_2SO_3.

(3) To 3 separate 200 ml portions of 0.75 M FBS add a known volume of 1.00 N NaOH, record the pH then determine Na_2SO_3 and HCHO.

(4) Calculate the moles of NaOH consumed as A-B and/or A-B[1] where:

A = moles OH^- added = liters NaOH added x molarity
B = moles free OH^- = (OH^-) from pH $\left(\frac{\text{moles}}{\text{liter}}\right)$ x total solution volume (liters)
B^1 = moles free OH^- = liters NaOH added to titrate distilled water to same pH x molarity

(5) Calculate the moles of Na_2SO_3 and HCHO formed where:

moles Na_2SO_3 or $HCHO_{formed}$ = moles/liter (from analysis) x total solution volume (liters)

4.6.3 Test Results:

Figure 4.6.1 shows the alkaline titration curves for 200 ml of 0.100 M FBS

and 200 ml of distilled water. Figure 4.6.2 shows the portion of the alkaline titration curve of 0.75 M FBS that includes the points at which Na_2SO_3 and HCHO determinations were made. Figure 4.6.3 is an acid/base titration curve of 0.10 M Na_2SO_3 shown for comparison.

Table 4.6.1 gives the data obtained on the three samples using 0.10 M FBS. Table 4.6.2 gives the data obtained on the three samples using 0.75 M FBS. Table 4.6.3 summarizes the ratio of moles OH^- consumed to moles of $SO_3^=$ and HCHO generated in both tests.

TABLE 4.6.1
(200 ml 0.10 M FBS)

SAMPLE	ml 1.0 M NaOH Added	pH	(Na_2SO_3)	moles Na_2SO_3 generated	moles OH^- consumed (from pH)	moles OH^- consumed (from water titration)
1A	6.00	11.44	0.0190	0.00391	0.0054	0.0054
2A	14.00	12.04	0.0329	0.00705	0.0117	0.0116
3A	20.00	12.32	0.0383	0.00843	0.0154	0.0152

TABLE 4.6.2
(200 ml 0.75 M FBS)

SAMPLE	ml 1.0 M NaOH Added	pH	(HCHO)	(Na_2SO_3)	moles Na_2SO_3 Generated	moles HCHO Generated	moles OH^- consumed (from pH)
1B	4.00	9.89	0.0135	0.0157	0.00320	0.00276	0.0040
2B	6.70	10.23	0.0196	0.0229	0.00473	0.00405	0.0065
3B	10.70	10.50	0.0280	0.0319	0.00621	0.00590	0.0104

TABLE 4.6.3

SAMPLE	$\frac{\text{moles } OH^- \text{ Consumed}}{\text{moles } SO_3^= \text{ Generated}}$	$\frac{\text{moles } OH^- \text{ Consumed}}{\text{moles HCHO Generated}}$
1A	1.38	-
2A	1.66	-
3A	1.83	-
1B	1.25	1.44
2B	1.37	1.60
3B	1.68	1.76

4.6.4 Conclusions:

The data indicate that:

(1) The total OH^- added cannot be accounted for by summing free OH^- and the amount of $SO_3^=$ or HCHO generated.

(2) The free OH^- concentration computed from pH values is in agreement with values obtained by NaOH titration of distilled water.

(3) We are unable to obtain an inflection point in the alkaline titration of FBS in aqueous solution.

(4) Alkaline titration of FBS cannot be considered analogous to neutralizing an equivalent amount of $NaHSO_3$ (Figure 4.6.3). Sulfite evidently is released from the complex as $SO_3^=$ and not as HSO_3^-.

I really don't know how to interpret this data. The implications are extremely pertinent to any attempt at accounting for alkalinity loss in developers containing FBS. This would appear to be a hopeless task when we can't account for it in an alkaline titration of FBS.

The most apparent conclusion is that our model (Equation 3.2) is not fully descriptive. This equation reversed is, however, precisely the equation used in determining formaldehyde content and is entirely dependent on one mole of formaldehyde being equivalent to one mole of hydroxide. The analysis procedure does, however, require an excess of sulfite to achieve a quantitative yield of hydroxide.

Some possible interpretations of the data might conclude that:

(A) The Na_2SO_3 and HCHO determinations are not valid. This interpretation would certainly be subject to substantiating data as much of this work indicates that the Na_2SO_3 and HCHO determinations are reasonably precise and accurate. We should call attention to the fact that most of the work preceeding this section has dealt with the relationship of free OH^-, $SO_3^=$ and HCHO existing at equilibrium and not necessarily to amounts reacting, etc. Equilibrium, of course, relates to active concentration and not necessarily to quantities consumed and/or generated. Examination of the data in this section will still show a consistent relationship between free OH^-, $SO_3^=$ and HCHO concentrations. The discrepancy is in the accountability of the added alkali.

(B) Free $SO_3^=$ and HCHO may have some acid/base buffer capacity over the pH range involved. To check this, we titrated 200 ml of 0.04 M Na_2SO_3 and HCHO solutions with 1.00 N NaOH. (A 0.04 M concentration was chosen because it slightly exceeds the maximum free Na_2SO_3 and HCHO concentration found in any of the preceeding tests.) Neither showed a measurable buffer capacity over the pH range from 9.5 to 12.5. That is, their titration curves over this pH range did not vary significantly from that of distilled water.

(C) Interionic attraction and solvation of ions is such that a portion of the added OH^- is always present in some intermediate form (neither as free OH^- nor as reaction products). We are dealing with reasonably strong electrolytes that are interpreted as being completely dissociated into ions, but at higher concentrations these ions appear to be associated by interionic attraction and solvation into ion pairs or undissociated molecules.

My opinion is that the latter interpretation is the most probable. I would not want to speculate as to possible intermediate forms or to the possible effect of excess sulfite in such a situation.

In any respect, the data show that we are unable to account for a large portion of the OH^- added to FBS solutions. This fact alone makes it impossible to satisfy the third goal of this project.

Figure 4.6.1

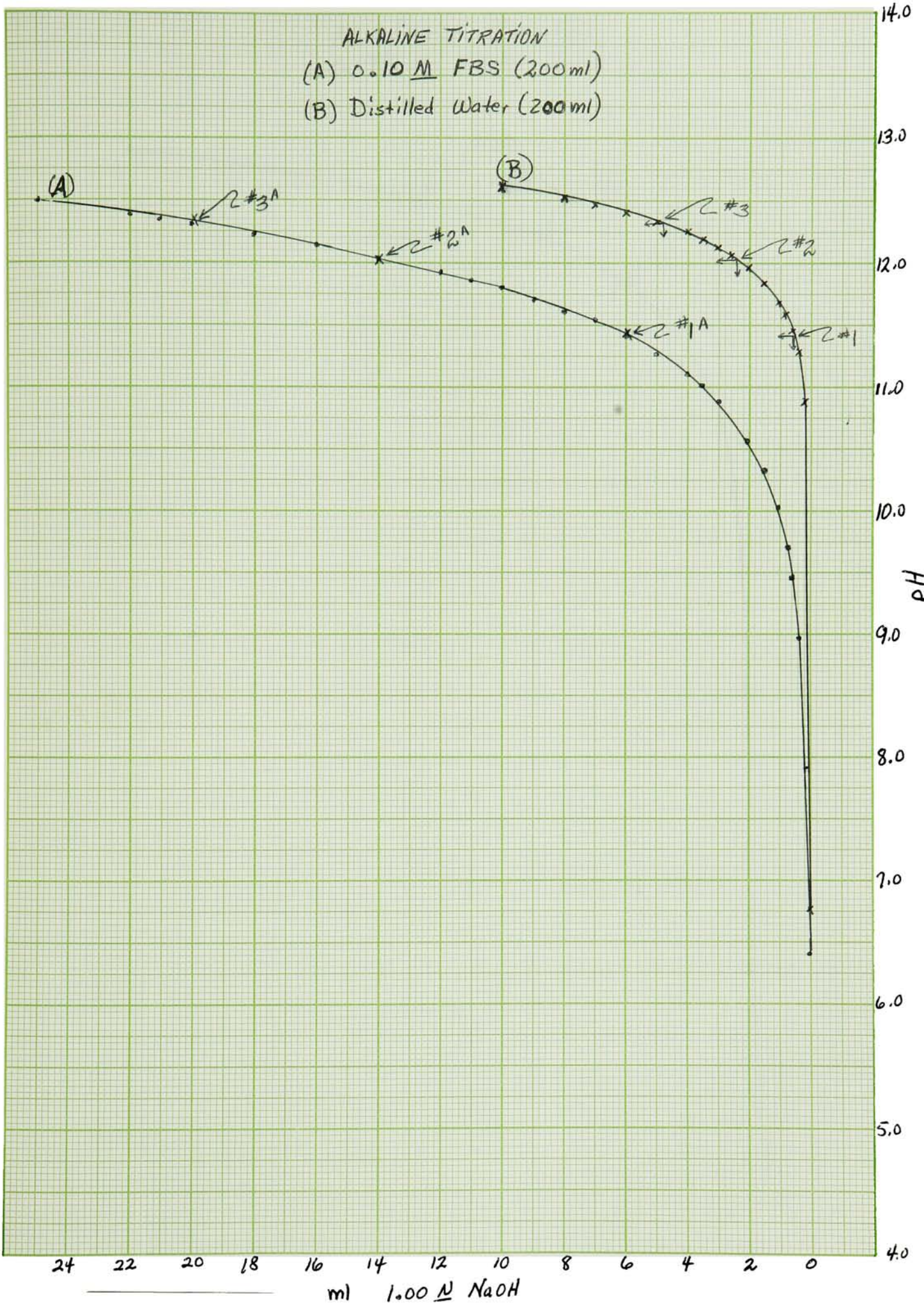

ALKALINE TITRATION
(A) 0.10 M FBS (200 ml)
(B) Distilled Water (200 ml)
(A)
(B)
#3A
#2A
#1A
#3
#2
#1
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
pH
24
22
20
18
16
14
12
10
8
6
4
2
0
ml 1.00 N NaOH

Figure 4.6.2

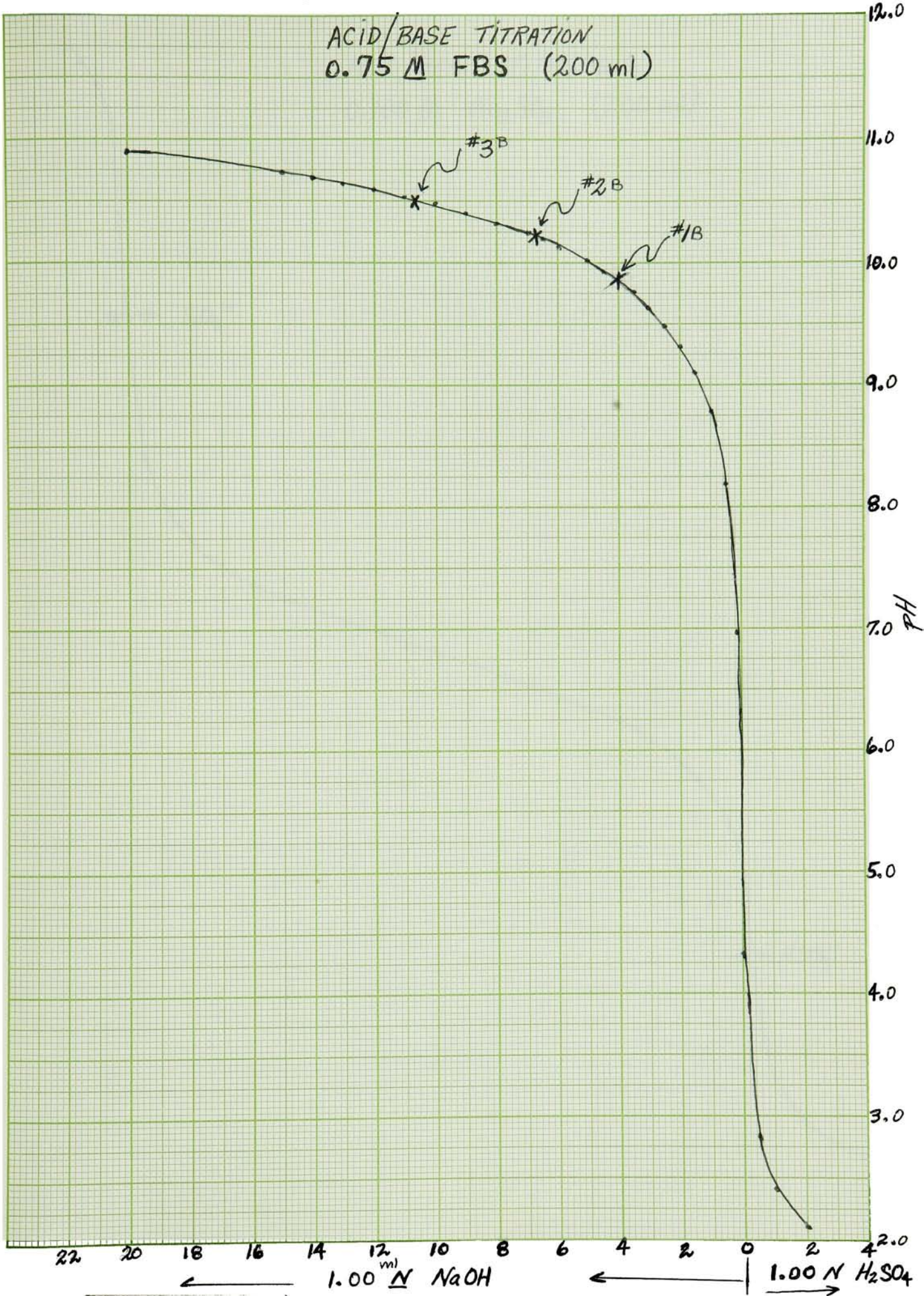
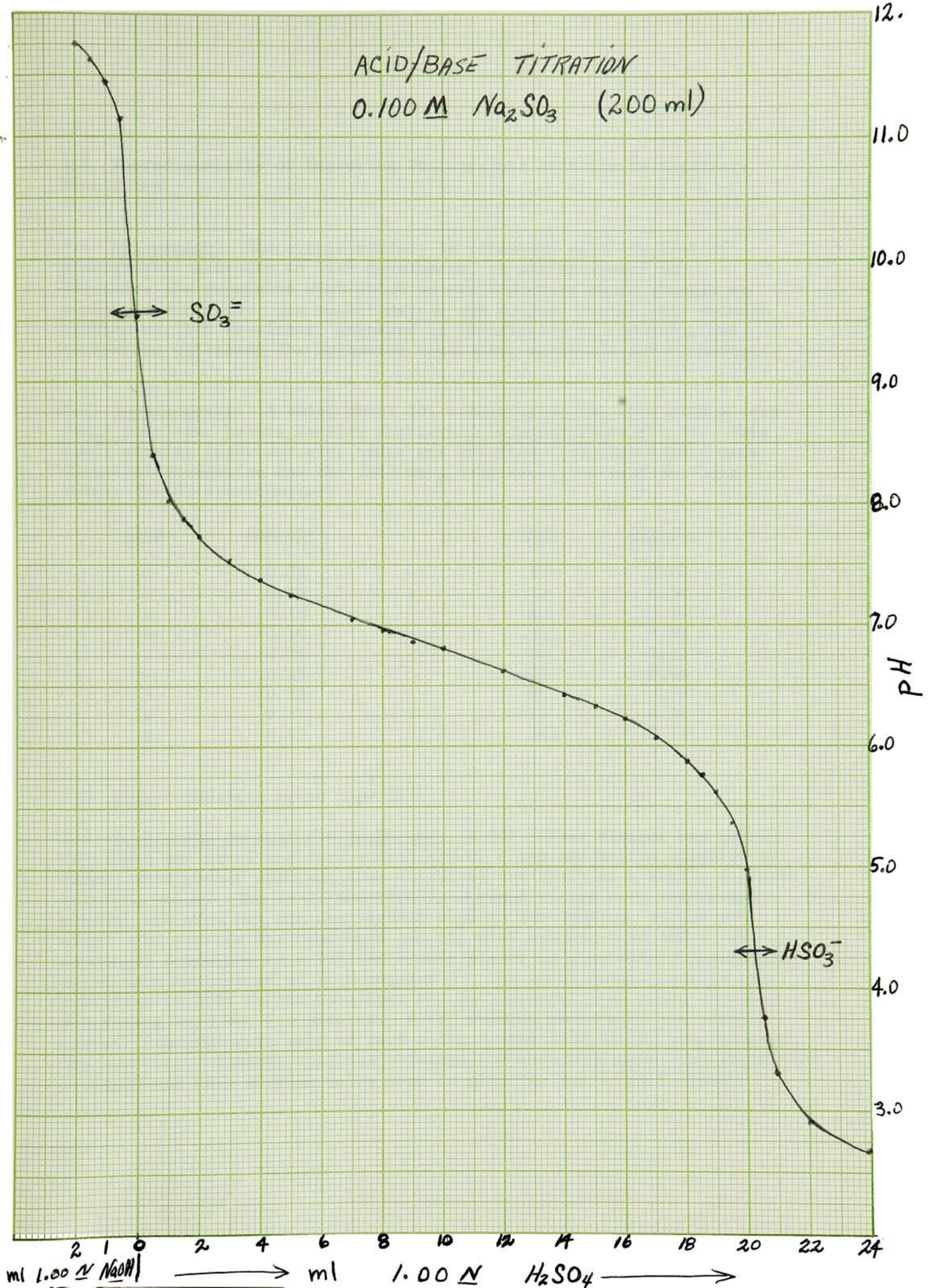

ACID/BASE TITRATION
0.75 M FBS (200 ml)
#3B
#2B
#1B
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
pH
22
20
18
16
14
12
10
8
6
4
2
0
2
4
1.00 (ml) N NaOH
1.00 N H2SO4

Figure 4.6.3


ACID/BASE TITRATION
0.100 M Na_2SO_3 (200 ml)
$SO_3^=$
HSO_3^-
pH
12.
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2 1 0 2 4 6 8 10 12 14 16 18 20 22 24
ml 1.00 N NaOH
ml 1.00 N H_2SO_4

5.0 Reproducibility of Measuring Photographic Activity in Replicate Developers

5.1 Discussion: Since this project is concerned with the loss of photographic activity in lith developers, it was necessary to determine the precision with which we could measure these changes in developer activity. The sensitometric and process variability between batches of lith developer, prepared as identically as possible, was determined utilizing the following equipment, materials and technique:

5.2 Sensitometry: A Kodak Model 101 sensitometer was used with a step wedge modulator having density increments of approximately 0.05. This small density increment step wedge was obtained from the Graphic Arts Technical Foundation and the following step densities read on their McBeth TD-102 densitometer:

Step	Density	Step	Density
1	0.05	10	0.46
2	0.10	11	0.50
3	0.15	12	0.55
4	0.19	13	0.59
5	0.24	14	0.62
6	0.29	15	0.66
7	0.33	16	0.70
8	0.37	17	0.74
9	0.42	18	0.77

5.3 Film: Kodalith Ortho Type III

5.4 Developing Apparatus & Technique: A #15 rubber stopper was ground to remove the bevel and form a disk having a top and bottom diameter of 82mm. This rubber disk was then fitted to the shaft of a small, electric stirring motor. Two sensitometrically exposed strips were then simply pinned, emulsion out and the lighter exposed end leading, around the disk. The stirrer was hand-held and the disk submerged in 500 ml of developer contained in a 1-liter beaker placed in a constant temperature water bath maintained at 26.0 degrees C. The sensitometric strips were permitted to stir in the developer for 3.25 minutes then fixed in Kodak F-5 fixing bath for 1.5 minutes. After washing and drying the strips, density readings were made of each strip on the GATF TD-102 densitometer. The two output density readings obtained for each modulator step were averaged and this average value used in plotting the D-Log E curve.

5.5 Developer Preparation: Four individual 500 ml batches of unbuffered lith developer were prepared by dissolving 33.5 grams of sodium formaldehyde bisulfite and 5.50 grams of hydroquinone in about 400 ml of distilled water. 0.5 gram of potassium bromide was added by pipetting 2.5 ml of a 20% (W/V) KBr solution into the developer. The developer was diluted to 500 ml in a volumetric flask then transferred to a 1-liter beaker. 6.0M NaOH was then added by buret until a pH of 10.00 (later changed to 10.20) was obtained. This required about 6 ml of 6.0 M NaOH. The additional dilution of the developing agent by this amount was ignored because it was essentially constant from batch to batch and, in later work, the actual developing agent concentration was determined by analysis.

5.6 Test Results: The results obtained on the four initial developer preparations are shown by the D-Log E plots in Figure 5.6. Using the ASA criterion for lith film speed, (the log exposure corresponding to a density of 2.50) the maximum variability between developer batches is approximately 0.03 Δ Log E. (Note that the Log E scale is expanded 4 times as draw.) This degree of inherent process variability is adequate for the purposes of the project and no other work was done solely to determine process variability. However, during subsequent work, there were occasions where replicate fresh developers were prepared and their activity sensitometrically monitored. A record was kept of the ASA speed obtained in each case and the results summarized in Table 5.6 along with the results on the four initial developers.

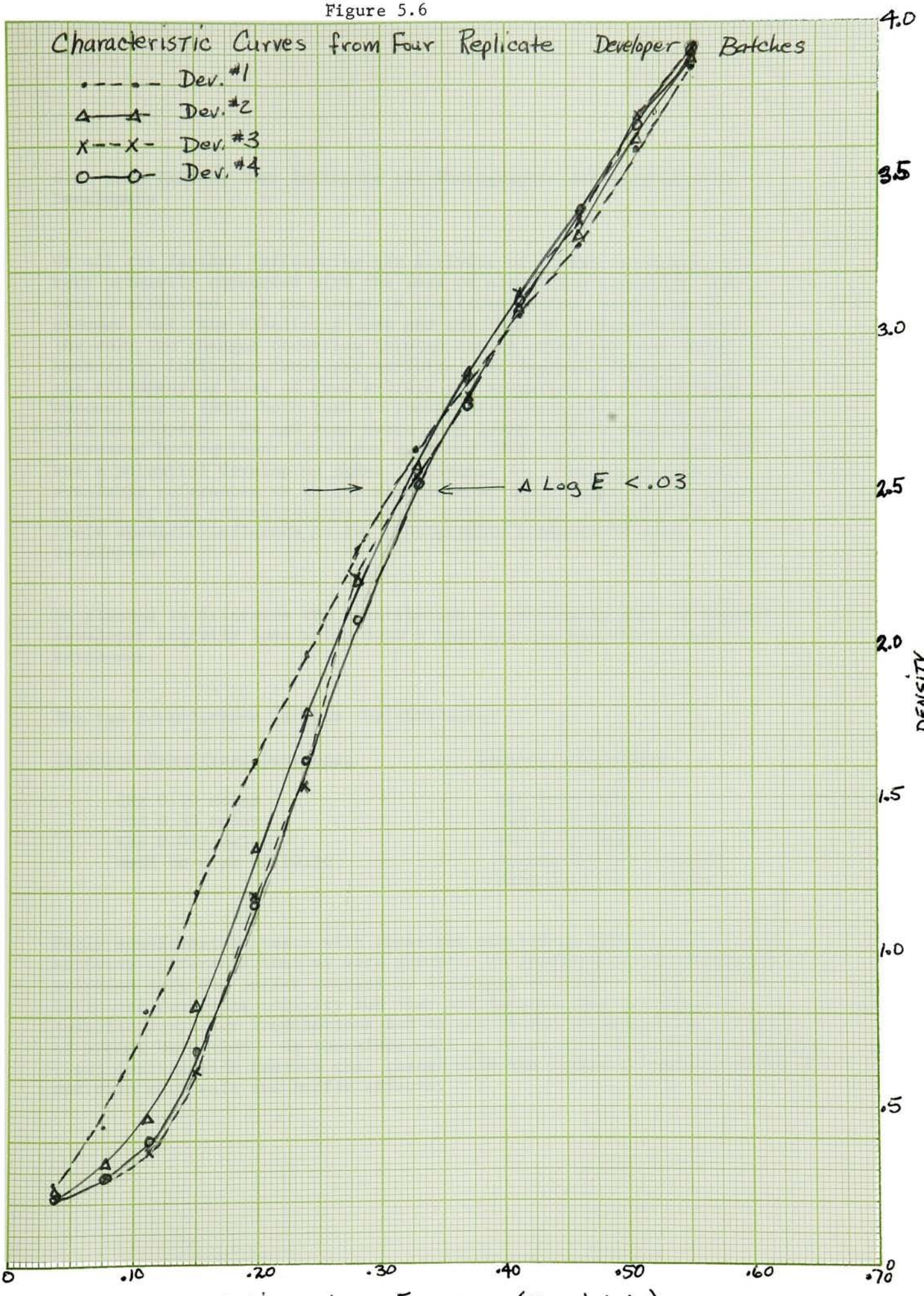
TABLE 5.6

ASA SPEED ON INDIVIDUAL DEVELOPER PREPARATIONS

Developer	Initial Unbuffered Developer pH = 10.00 KBr = 1.0 g/1 dev. time - 3.25 minutes	Standard Unbuffered Developer pH = 10.20 KBr = 2.0 g/1 dev. time - 3 minutes	Carbonate Developer pH = 10.20 KBr = 2.0 g/1 dev. time - 1.5 minutes
	0.305 Log E	0.315 Log E	0.82 Log E
	0.315 Log E	0.305 Log E	0.80 Log E
	0.315 Log E	0.305 Log E	0.80 Log E
		0.295 Log E	
	0.330 Log E	0.325 Log E	
		0.320 Log E	
	Log $\overline{E}$ = 0.316	Log $\overline{E}$ = .309	Log $\overline{E}$ = .807

5.7 Conclusion: The above data has a standard deviation of 0.01. Developer activity changes $\geq$ 0.05 Log E are, therefore, readily detectable with the sensitometric and development methods employed.

Figure 5.6


Characteristic Curves from Four Replicate Developer Batches
Dev. #1
Dev. #2
Dev. #3
Dev. #4
Δ Log E < .03
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0
DENSITY
0
.10
.20
.30
.40
.50
.60
.70
Relative Log Exposure (Expanded 4X)

6.0 Some Factors That Influence the Photographic Activity of Lith Developers

Of all the factors influencing the activity of a lith developer, we were primarily concerned with the loss of alkalinity resulting from aerial oxidation. As mentioned in the introduction, we initially assumed that this alkalinity loss and the loss of hydroquinone were the only two changes occurring through aerial oxidation that would measurably influence developer activity. We learned, however, that the accompanying loss of free sulfite and formation of hydroquinone monosulfonate (HQS) both tend to increase the activity of oxidized lith developers. We had been aware that lower sulfite concentrations increased hydroquinone developer activity (reference 6) and that HQS was a potential developing agent (reference 7). But there were no available references as to the magnitude of the changes occuring in sulfite or HQS concentrations during normal aerial oxidation or to their specific influence on the photographic activity of lith developers.

We planned to determine the contribution of alkalinity loss to overall developer activity loss using both a buffered and unbuffered lith developer.

The two formulations adopted for this were:

Standard-Unbuffered Developer

QH_2 0.10 molar
FBS 0.50 molar
KBr 0.017 molar
NaOH to a pH of 10.20

Carbonate Developer

QH_2 0.10 molar
FBS 0.50 molar
KBr 0.017 molar
$Na_2CO_3 \cdot H_2O$ 0.50 molar
NaOH to a pH of 10.20

Early sensitometric tests with these two developers showed such a large activity difference that we were prompted to investigate the influence of solution salt and buffer content on developer activity. Both factors influence developer activity but they are factors that are fixed in specific developer formulations and do not change materially as a result of aerial oxidation. We therefore want to treat this section in two parts; first dealing with factors that change with the degree of aerial oxidation and then with salt and buffer effects.

6.1 Factors Influencing Activity That Change with the Degree of Aerial Oxidation

6.1.1 The Influence of Free Sulfite Concentration:

6.1.1.1 Discussion: The purpose of this experiment was to determine the developer activity change caused by changing the free sulfite concentration. Specifically, we wanted to know if decreases in the free sulfite concentration, over the range expected in later aerial oxidations experiments (from $\approx$ 2.0 g/l to $\approx$ 0.5 g/l) would have sufficient influence on developer activity that it would have to be compensated for when attempting to measure the influence of alkalinity and hydroquinone loss.

6.1.1.2 Test Plan: Prepare one liter of standard unbuffered developer. Determine the free sulfite concentration. Using a 500 ml portion of the developer, develop sensitometric strips for 3 minutes at 26 degrees C. Add 1.50 grams of reagent grade sodium sulfite to the same 500 ml of developer (readjust to original pH if necessary). Determine the free sulfite concentration. Process sensitometric strips.

To the other 500 ml portion of the developer, add formaldehyde equivalent to approximately 0.38 grams (readjust to original pH if necessary). Determine the free sulfite concentration and process sensitometric strips.

6.1.1.3 Test Results: The free sulfite concentrations were found to be:

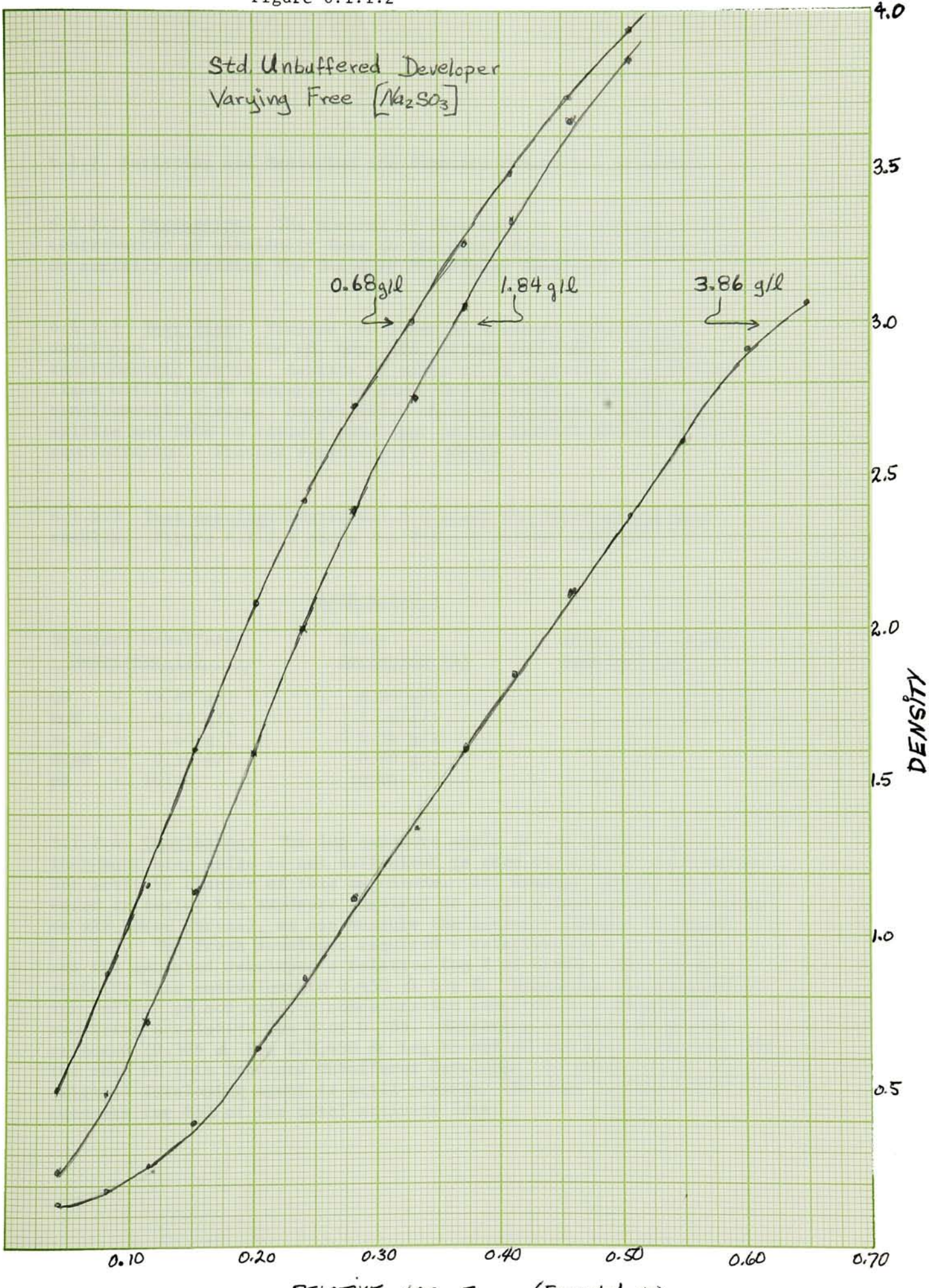
1.84 g/l Standard Unbuffered Developer
3.86 g/l (after Na_2SO_3 addition)
0.68 g/l (after HCHO addition)

Figure 6.1.1.2 shows the D-Log E curves obtained at the three levels of free sulfite.

6.1.1.3 Conclusion: Increasing the free sulfite concentration from 1.84 g/l to 3.86 g/l results in decreased contrast and a loss of activity of about 0.23 Δ Log E. Decreasing the sulfite concentration from 1.84 g/l to 0.68 g/l results in an increase of activity of about 0.05 Δ Log E. This latter sulfite range is in the general range in which

we will be working with aerially oxidized developers; therefore, activity <u>increases</u> due only to changes in sulfite concentration can be expected to be of a magnitude of about 0.05 Δ Log E. In practical work, this could probably be ignored. In this project, however, we can measure an activity change of this magnitude and can compensate for it by sulfite additions. The decision then is that we should attempt to restore free sulfite to its initial concentration in experiments in which we are attempting to measure the influence of hydroquinone and alkalinity loss.

Figure 6.1.1.2


Std. Unbuffered Developer
Varying Free [Na_2SO_3]
0.68 g/l
1.84 g/l
3.86 g/l
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
DENSITY
0.10
0.20
0.30
0.40
0.50
0.60
0.70
RELATIVE LOG E (Expanded 4x)

6.1.2 Aeriating and Restoring the Standard Unbuffered Developer

6.1.2.1 Discussion: The purpose of this test is to determine the contribution of alkalinity loss to the total developer activity loss on aerially oxidizing the Standard Unbuffered developer.

6.1.2.2 Test Plan: Prepare one liter of Standard Unbuffered developer. Analyze for pH, QH_2, HQS, Na_2SO_3 and HCHO. Process sensitometric strips. Aeriate by means of an aspirator and vacuum flask until the pH decreases by about 0.2 pH units. Process sensitometric strips. Repeat above chemical analyses. Add free sulfite and NaOH to restore developer to its initial pH and sulfite concentration. Process sensitometric strips.

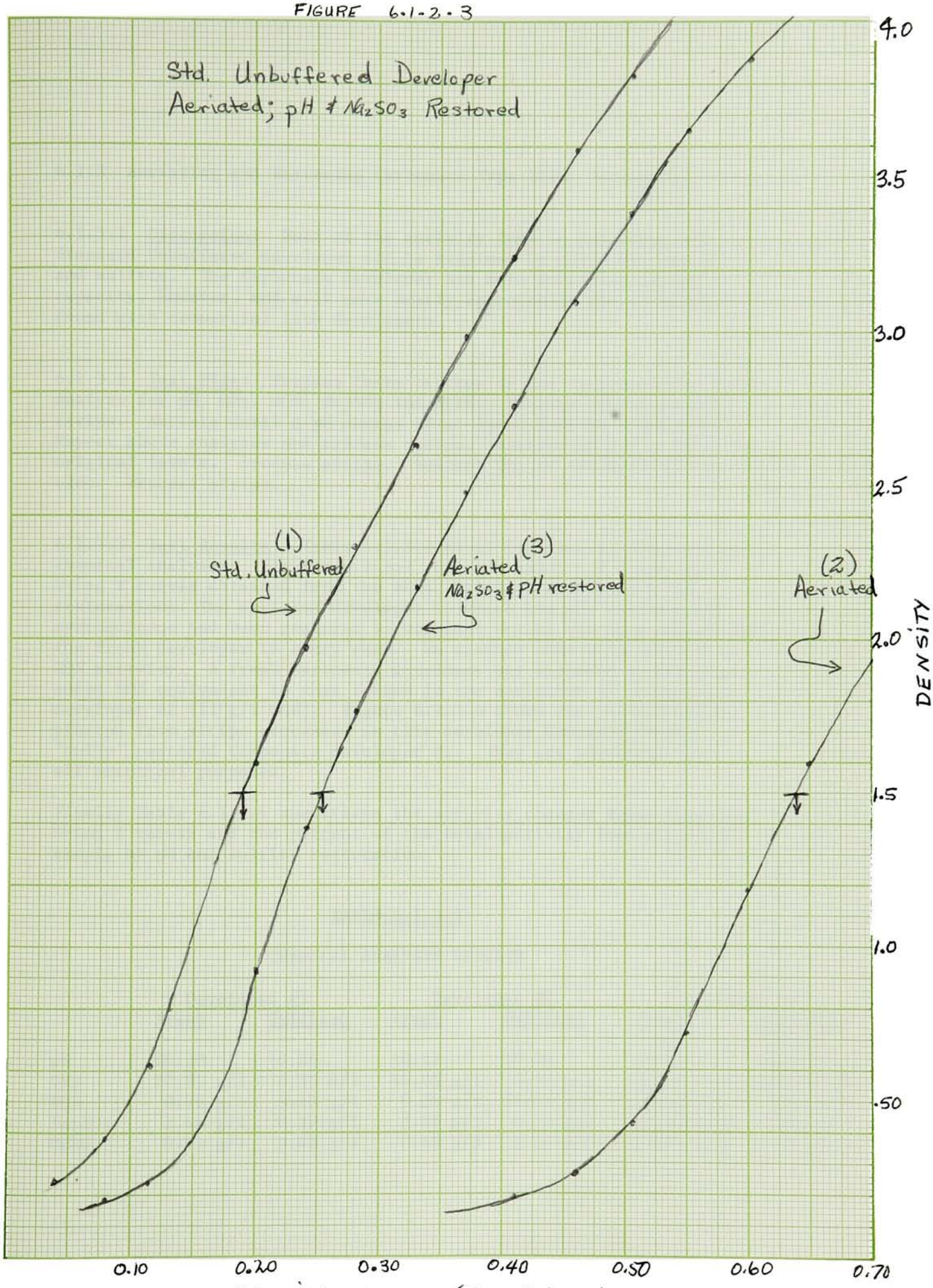
6.1.2.3 Test Results: Table 6.1.2.3 gives the chemical analysis results. Figure 6.1.2.3 shows the D-Log E curves obtained.

TABLE 6.1.2.3

Standard Unbuffered Developer (1)	After Aeriating (2)	After pH & Na_2SO_3 Restored (3)
QH - 10.80 g/1	8.33 g/1	-
HQS - 0.31 g/1	5.26 g/1	-
Na SO - 1.80 g/1	0.54 g/1	1.92 g/1
HCHO - 0.39 g/1	0.98 g/1	-
pH - 10.20	10.04	10.20

6.1.2.4 Conclusion: The log exposure scale of the small density increment step wedge is not sufficient to show the full D-Log E curves for activity changes of this magnitude. If, however, we use as a speed criterion the exposure required to yield a density of 1.5 (shown on all three curves), we can measure the activity changes in Figure 6.1.2.3. The fresh developer required a relative Log E of 0.190 and the aeriated developer a relative Log E of 0.640. This is an activity loss equivalent to 0.450 Δ Log E. Restoring the solution to its initial pH and sulfite concentration resulted in a developer requiring a relative Log E of 0.255. Restoring sulfite and pH then restored (0.385 Δ Log E/0.450 Δ Log E) 85% of the lost activity. In the case of this Standard Unbuffered developer, in which 77% of the original developing agent is still present, the loss in alkalinity accounts for 85% of the total activity loss.

FIGURE 6.1-2-3


Std. Unbuffered Developer
Aeriated; pH & Na_2SO_3 Restored
(1)
Std. Unbuffered
(3)
Aeriated
Na_2SO_3 & pH restored
(2)
Aeriated
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.50
DENSITY
0.10
0.20
0.30
0.40
0.50
0.60
0.70
RELATIVE LOG E (Expanded 4X)

6.1.3 Aeriating and Restoring Carbonate Type Lith Developers

6.1.3.1 Discussion: Most of the activity lost in aeriating the Standard Unbuffered developer can be regained by restoring the pH and sulfite. The Carbonate developer has more acid-base buffer capacity, however, and will more nearly approximate the situation found with commercial lith developers.

6.1.3.2 Test Plan: Prepare three batches of the Carbonate developer. Analyze for pH, QH_2, HQS, Na_2SO_3 and HCHO. Process sensitometric strips. Aeriate until a pH change of at least 0.05 is indicated. Repeat above analyses and process strips. Restore pH and sulfite to original levels. Process strips. Restore QH_2 to original concentration. Process strips.

6.1.3.3 Test Results: Table 6.1.3.3 gives the results obtained by chemical analyses. Figures 6.1.3.3, 6.1.3.4 and 6.1.3.5 are the D-Log E curves obtained from the three developer aeriations and restorations. The aeriated developer in which the pH, sulfite and hydroquinone had been restored to original values was more active than the fresh developer in every case. We assumed that this was due to HQS activity. A fresh Carbonate developer was prepared to which we added HQS equivalent to that formed in the aeriation of Carbonate developer #2 (11 g/l HQS). Figure 6.1.3.6 shows the D-Log E curve plotted from strips processed in this developer compared to the "fully" restored Carbonate developer #2. They are identical for all practical purposes.

Finally Table 6.1.3.4 summarizes the activity changed taken from the D-Log E curves and the percent of the total activity loss restored simply by pH and sulfite restoration.

TABLE 6.1.3.3

CHEMICAL ANALYSIS RESULTS

	Developer #1		Developer #2		Developer #3	
	Fresh	Oxidized	Fresh	Oxidized	Fresh	Oxidized
pH	10.20	10.06	10.21	10.04	10.20	10.14
QH_2	10.85 g/l	6.35 g/l	11.05 g/l	5.55 g/l	10.75 g/l	8.18 g/l
HQS	0.46 g/l	9.40 g/l	0.24 g/l	11.30 g/l	0.62 g/l	5.85 g/l
Na_2SO_3	2.44 g/l	0.27 g/l	2.39 g/l	0.26 g/l	2.30 g/l	0.63 g/l
HCHO	0.41 g/l	2.48 g/l	0.48 g/l	2.54 g/l	0.44 g/l	1.46 g/l

TABLE 6.1.3.4

	Developer #1	Developer #2	Developer #3
(1) Fresh	0.81 Log E	0.82 Log E	0.81 Log E
(2) Aeriated	1.38 Log E	1.54 Log E	1.04 Log E
(3) pH & SO_3 Restored	1.06 Log E	1.42 Log E	0.86 Log E
(4) pH, SO_3 & QH_2 Restored	0.75 Log E	0.66 Log E	0.72 Log E
(5) Δ Log E (2-1)	0.57	0.72	0.23
(6) Δ Log E (2-3)	0.32	0.12	0.18
% total activity loss restored by pH and $SO_3^=$ restoration (6)/(5)	56%	17%	78%

6.1.3.4 Conclusion: Restoring the pH and sulfite in an aeriated carbonate type lith developer restores from 17% to 78% of the lost activity. The 78% restored activity was found in the developer having undergone the least oxidation (76% of the original QH_2 concentration still available). This is the range of oxidation of most practical importance and may indicate that alkalinity loss is most significant during the early stages of oxidation. Certainly, during this time, the (HQS)/(QH_2) ratio is smaller and the HQS influence in counteracting developer activity loss is minimized.

I would have expected that restoring pH and sulfite in developers #1 and #2 would have restored nearer the same proportion of the total activity loss. I have no rational hypothesis to explain the rather wide difference in the percent activity restored by pH and sulfite in these two developers.

HQS activity ranges from 0.06 to 0.16 Δ Log E in these samples, using a density of 2.50 as the critical density for film speed determination. This may be a misleading criterion in this case as toe speed is evidently influenced to a greater extent. In developers #1 and #2, where there is substantial HQS formation, the contrast is obviously decreased. The contrast loss is most evident after hydroquinone is restored but it is noticeable in all of the curves. This may have practical implications in developed halftone dot characteristics and in lith developers designed for machine processing. HQS often reaches overflow equilibrium concentrations near 10 g/l in these developers.

Although most commercial lith developers have a greater acid-base buffer capacity than the Carbonate developer used in these tests, the magnitude of activity change here attributable to alkalinity loss is sufficient to be a factor even in the most strongly buffered developers.

In summary, when a lith developer is aeriated:

(1) The free sulfite concentration decreases resulting in a slight increase in developer activity.

(2) QH_2 is oxidized to HQS and the HQS generated compensates somewhat for the activity lost through decreased QH_2.

(3) The pH decreases resulting in additional loss of activity that, on the basis of these tests, is a very significant part of the overall activity loss.

FIGURE 6-1-3-3

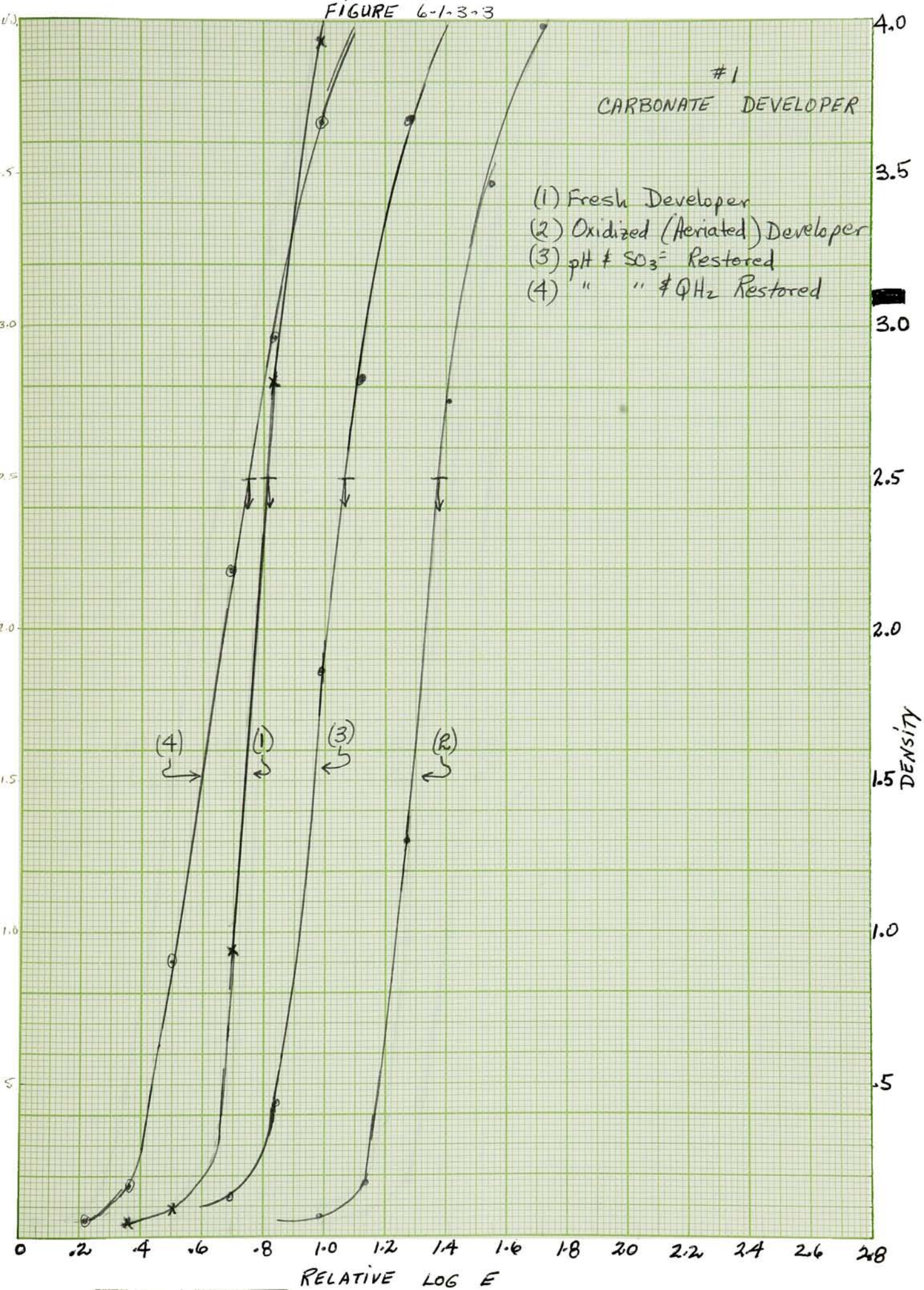

#1
CARBONATE DEVELOPER
(1) Fresh Developer
(2) Oxidized (Aeriated) Developer
(3) pH & $SO_3^=$ Restored
(4) " " & QH_2 Restored
(4)
(1)
(3)
(2)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
DENSITY
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
RELATIVE LOG E

FIGURE 6-1-3-4

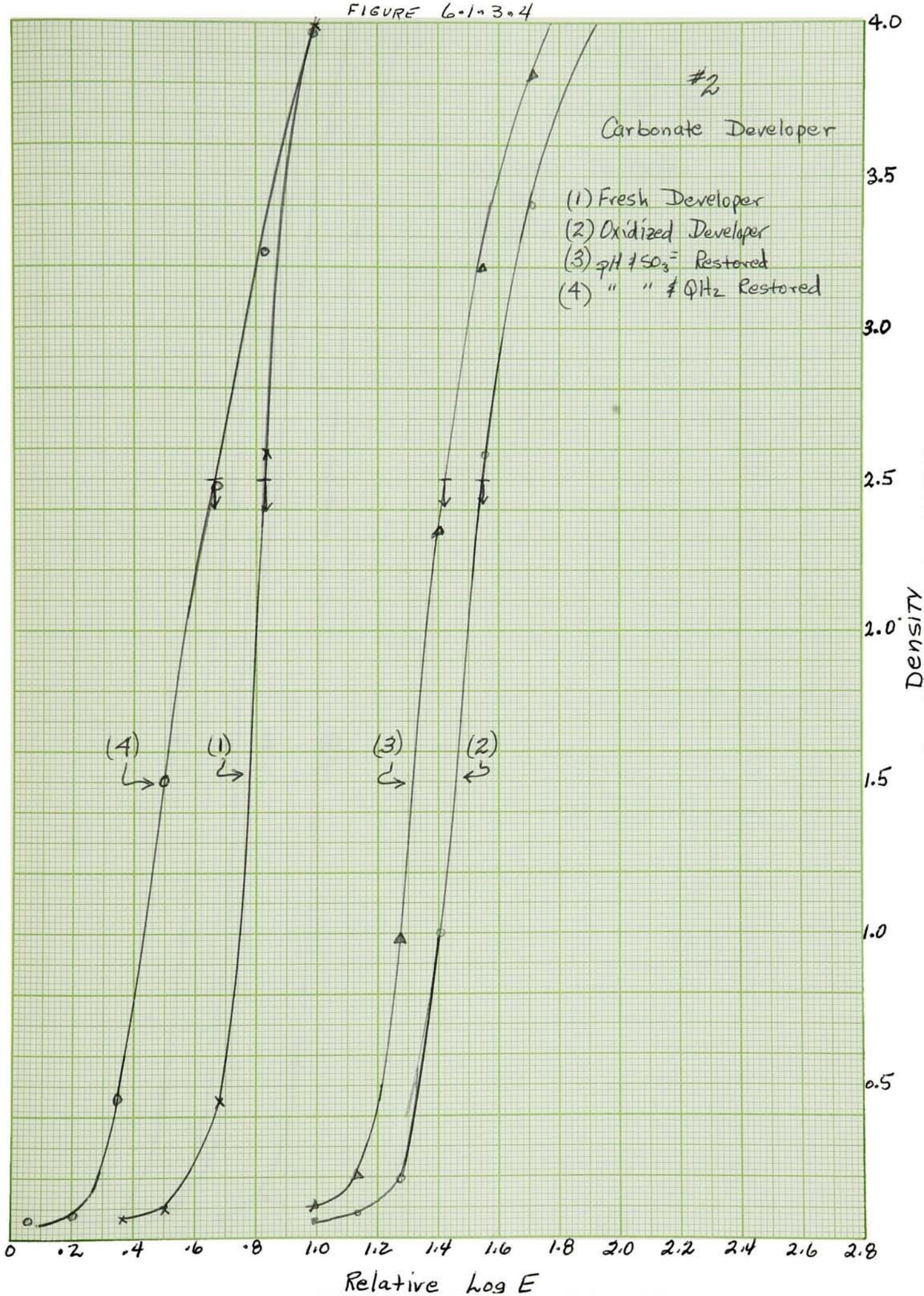

#2
Carbonate Developer
(1) Fresh Developer
(2) Oxidized Developer
(3) pH + $SO_3^=$ Restored
(4) " " + QH_2 Restored
(4)
(1)
(3)
(2)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Density
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Relative Log E

FIGURE 6.1.3.5

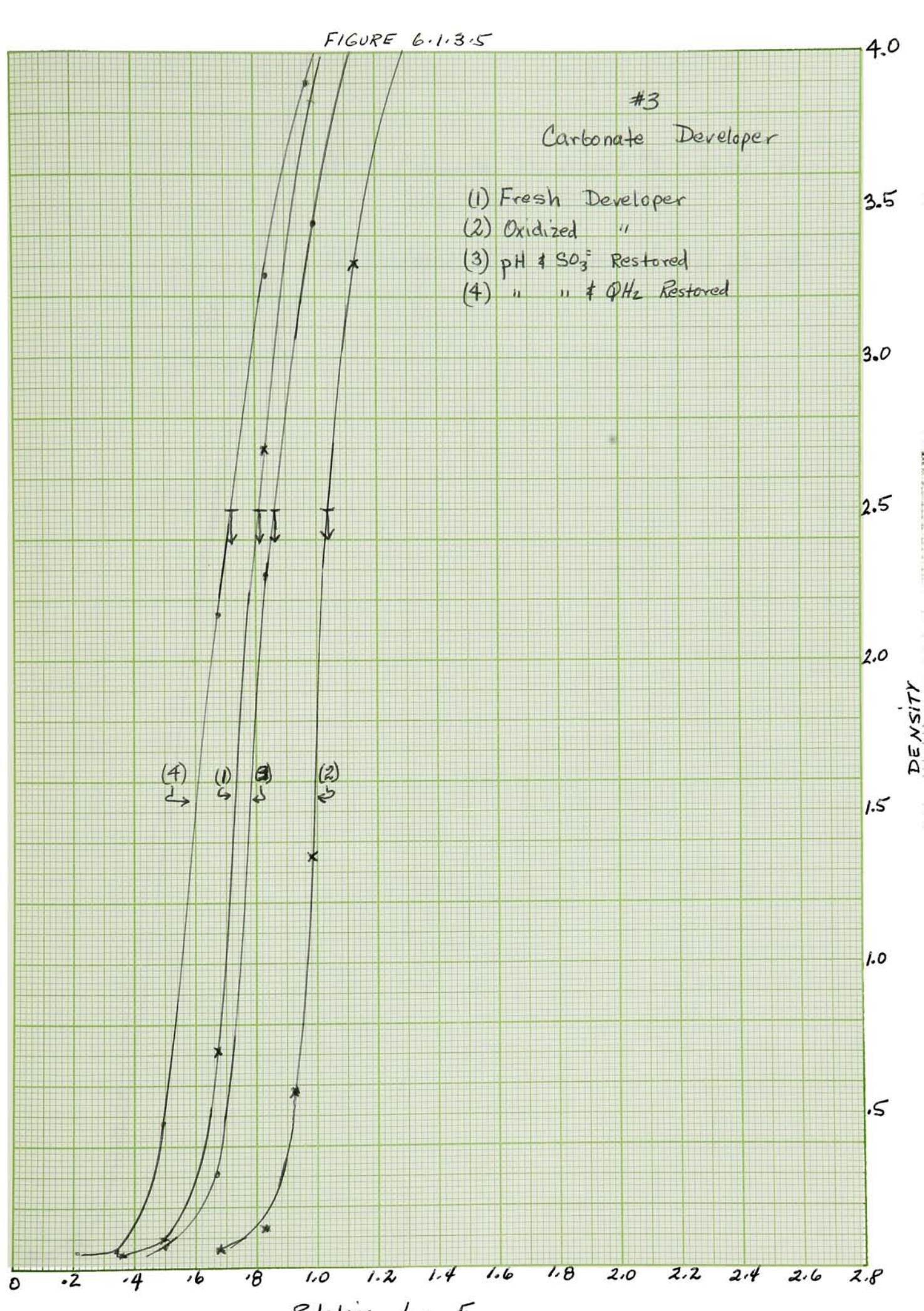
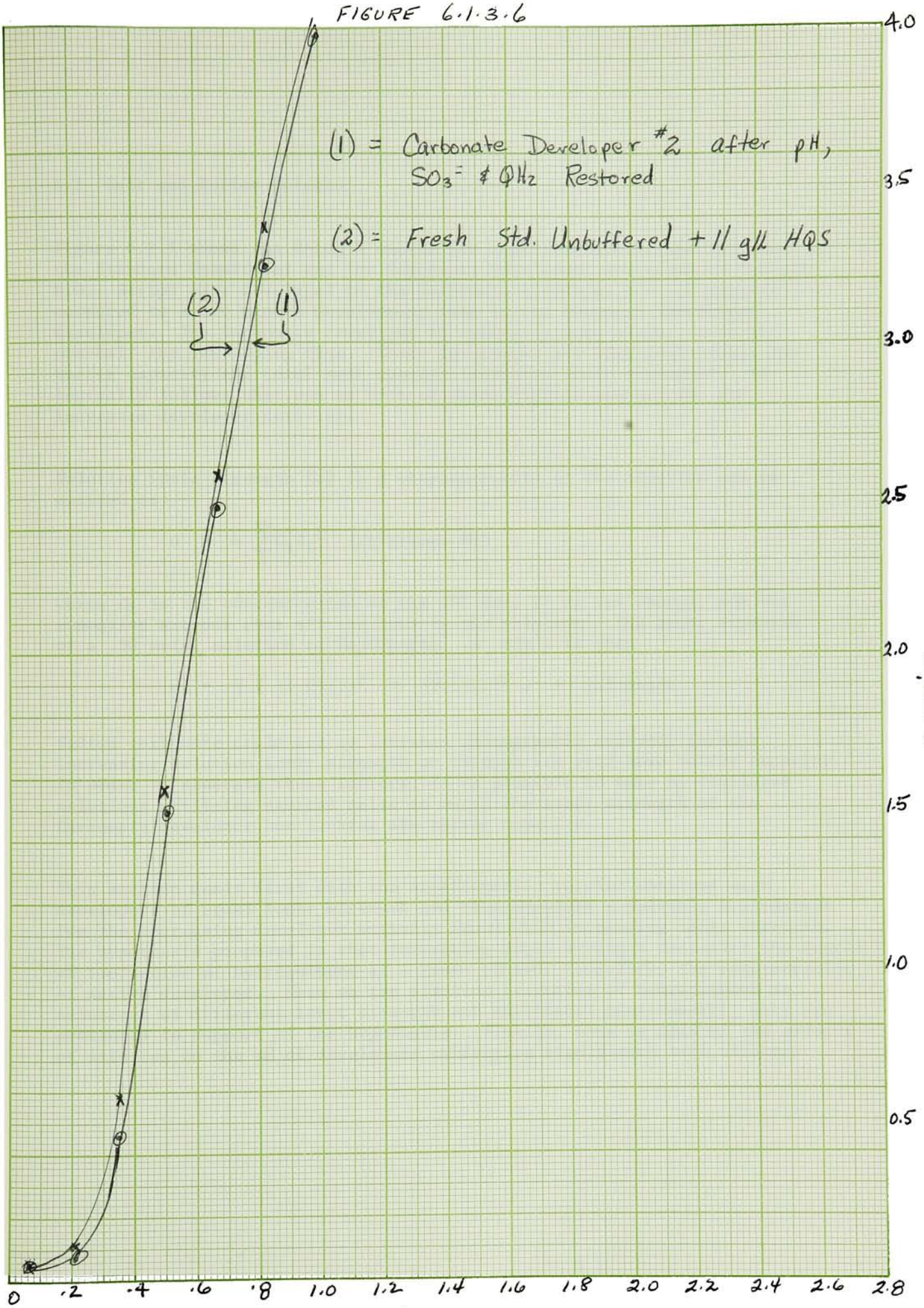

#3
Carbonate Developer
(1) Fresh Developer
(2) Oxidized "
(3) pH & $SO_3^=$ Restored
(4) " " & QH_2 Restored
(4)
(1)
(3)
(2)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
DENSITY
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Relative Log E

FIGURE 6.1.3.6


(1) = Carbonate Developer #2 after pH, $SO_3^=$ & QH_2 Restored
(2) = Fresh Std. Unbuffered + 11 g/L HQS
(2)
(1)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
DENSITY
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Relative Log E

6.2 Salt and Buffer Effects

Figure 6.2.1 shows the D-Log E curves for sensitometric strips developed in the Standard Unbuffered and the Carbonate developers described in Section 6.0. Strips were developed in the Carbonate developer for 1.5 minutes compared to a 3.0 minute development time in the Standard Unbuffered developer. The Carbonate developer is evidently more active, even at one-half the developing time. These developers are identical except for buffer capacity and total salt content (solution ionic strength). It logically follows that one or both of these factors account for the increased developer activity.

Solution ionic strength (u) is a characteristic of the solution and is defined as:

$$u = \tfrac{1}{2} \sum_{i} C_i Z_i^2 \quad \text{(reference \#8)}$$

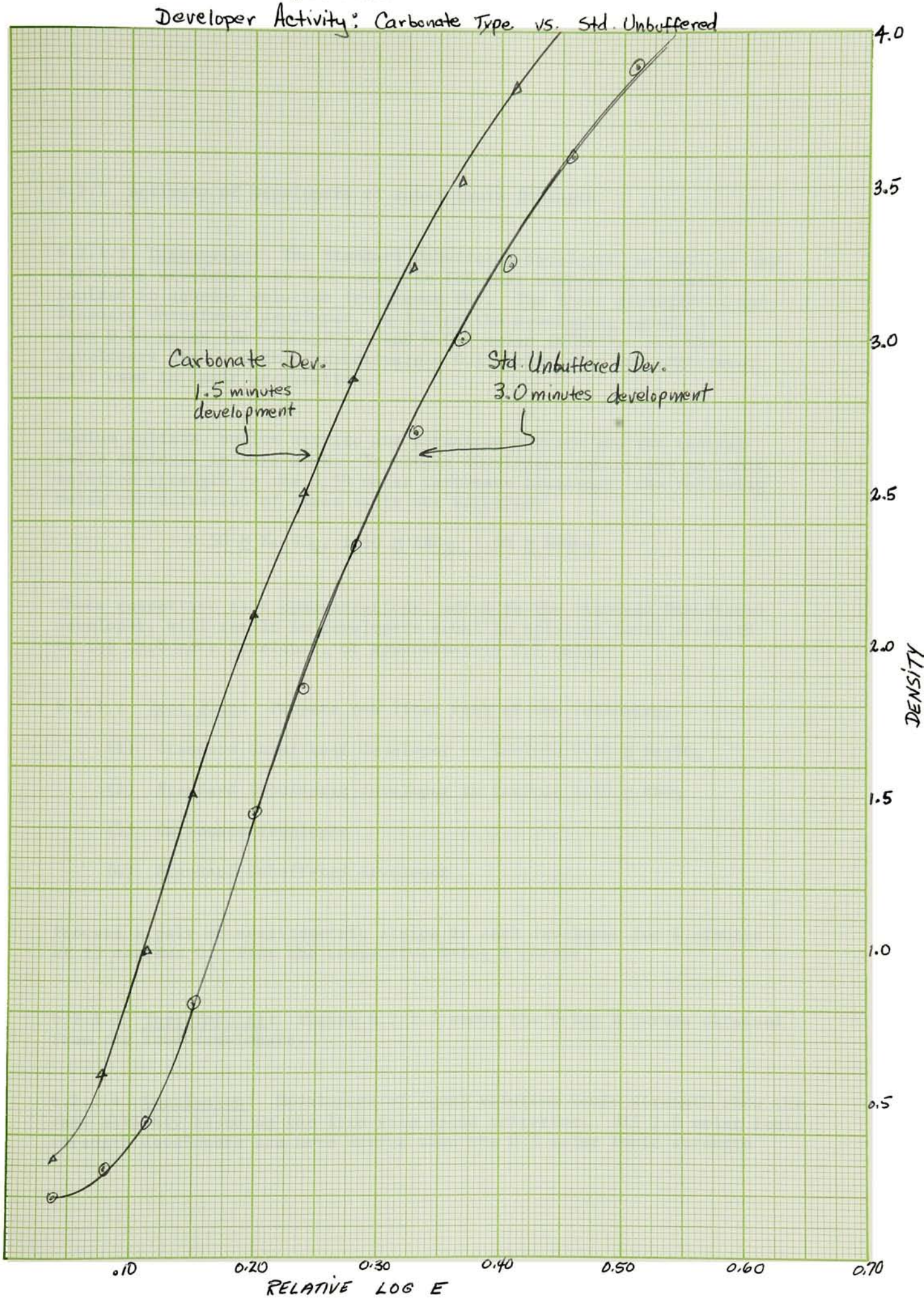
where C_i is the concentration of the i^{th} ion, Z_i is its charge, and the summation extends over all the ions in the solution. The ionic strength of a .50 molar solution of Na_2CO_3 ($2Na^+$ & $CO_3^=$) is then

$$u = \tfrac{1}{2} \left((1.0)(1)^2 + (0.5)(2)^2 \right) = 1.5 \text{ molar}$$

Sodium carbonate could act to increase photographic activity through increasing solution ionic strength or through its acid-base buffer capacity. In order to separate these factors, it is possible to make up developer solutions utilizing neutral salts to match the ionic strength of the Carbonate developer but lacking its buffer capacity.

This section deals first with the sensitometric results obtained with developers of equal ionic strength and then proposes a possible explanation for the increasing developer activity found with increasing ionic strength. The hypothesis proposed is that increasing ionic strength increases the degree of ionization of hydroquinone at a given pH and, therefore, the concentration of active developer. Data on the alkaline titration of hydroquinone in solutions of different ionic strength and additional sensitometric data are presented in support of the hypothesis. Finally, note is made of the effects of dilution on the pH of developers exhibiting significant salt effects.

Figure 6.2.1


Developer Activity: Carbonate Type vs. Std. Unbuffered
Carbonate Dev.
1.5 minutes
development
Std. Unbuffered Dev.
3.0 minutes development
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
DENSITY
.10
0.20
0.30
0.40
0.50
0.60
0.70
RELATIVE LOG E

6.2.1 Activity of Developers of Equal Ionic Strength

6.2.1.1 Discussion: The Standard Unbuffered developer, as well as the Carbonate developer, is 0.50 molar in FBS that supposedly is fully ionized in aqueous solution (reference #4). The ionic strength of the Standard Unbuffered developer, excluding the developing agent, is then 0.50 molar (Na^+ $HOCH_2SO_3^-$) and 0.017 molar (K^+Br^-). All the developers used are then approximately 0.52 molar plus any additional salt used in their preparation.

Sodium sulfate, sodium nitrate and potassium nitrate are the neutral salts employed in this work. To obtain developers equivalent in ionic solution strength to the 0.50 molar Carbonate developer, the following molar concentration of these salts are required:

$$0.50\ \underline{M}\ Na_2SO_4,\ 1.50\ \underline{M}\ KNO_3,\ 1.50\ \underline{M}\ NaNO_3$$

These respective salt concentrations, added to the Standard Unbuffered developer, will result in developers equal in solution ionic strength to the Carbonate developer, or approximately 2.0 molar.

6.2.1.2 Test Plan: Prepare one liter each of the following:

(1) Standard Unbuffered developer to include 0.50 $\underline{M}$ Na_2SO_4

(2) Standard Unbuffered developer to include 1.50 $\underline{M}$ KNO_3

(3) Carbonate developer

(4) Standard Unbuffered developer

Process a pair of sensitometric strips in each developer for 4 minutes at 23 degrees C. Plot the respective D-Log E curves.

6.2.1.3 Test Results: Figure 6.2.1.3 shows the D-Log E curves obtained from the four developers.

6.2.1.4 Conclusion: Developers of equal solution ionic strength show the same activity based on the lith film speed criterion. All 2.0 molar ionic strength developers are more active than the 0.5 molar ionic strength

Standard Unbuffered developer by about 0.30 Log E units. The developer prepared with sodium sulfate significantly deviates from the other two developers of equal ionic strength in the toe region of its D-Log E curve.

These results indicate that, under the developing conditions employed, solution ionic strength is a significant influencing factor in developer activity and buffer capacity is not.

Lith development, once initiated, proceeds very rapidly and one would expect that the acid/base buffer capacity would be very significant in maintaining the rapid developing rate. It may be that the influence of buffer capacity has been minimized by the relatively long developing time and high degree of agitation employed in this test. To better access the relative importance of buffer capacity, it seems advisable to run other tests at shorter developing times.

6.2.1.5 Test Plan: Prepare one liter of the Carbonate developer and one liter of the Standard Unbuffered developer to include 1.5 molar $NaNO_3$. Process pairs of sensitometric strips in each developer, decreasing the time of development from the preceding tests.

6.2.1.6 Test Results: Figures 6.2.1.4 and 6.2.1.5 show the D-Log E curves obtained from the two developers at developing times of 1.5 and 0.5 minutes respectively.

6.2.1.7 Conclusion: The increased buffer capacity of the Carbonate developer does not become a significant factor until developing times become very short. As would be expected, the buffer capacity has its most pronounced influence in the higher density areas.

These results, in summary, indicate that:

(1) Solution ionic strength has pronounced effects on lith developer activity.

(2) The developer buffer capacity is of no significance until the developing rate becomes diffusion limited.

(3) Equivalent results are obtained using either sodium or potassium salts.

(4) Sulfate appears to promote a longer toe on the D-Log E curve (an undesirable characteristic in lith developers). This conceivably is related to the sulfate ion's tendency to minimize emulsion swelling thereby providing a shorter diffusion path for the developing agent.

Figure 6.2.1.3

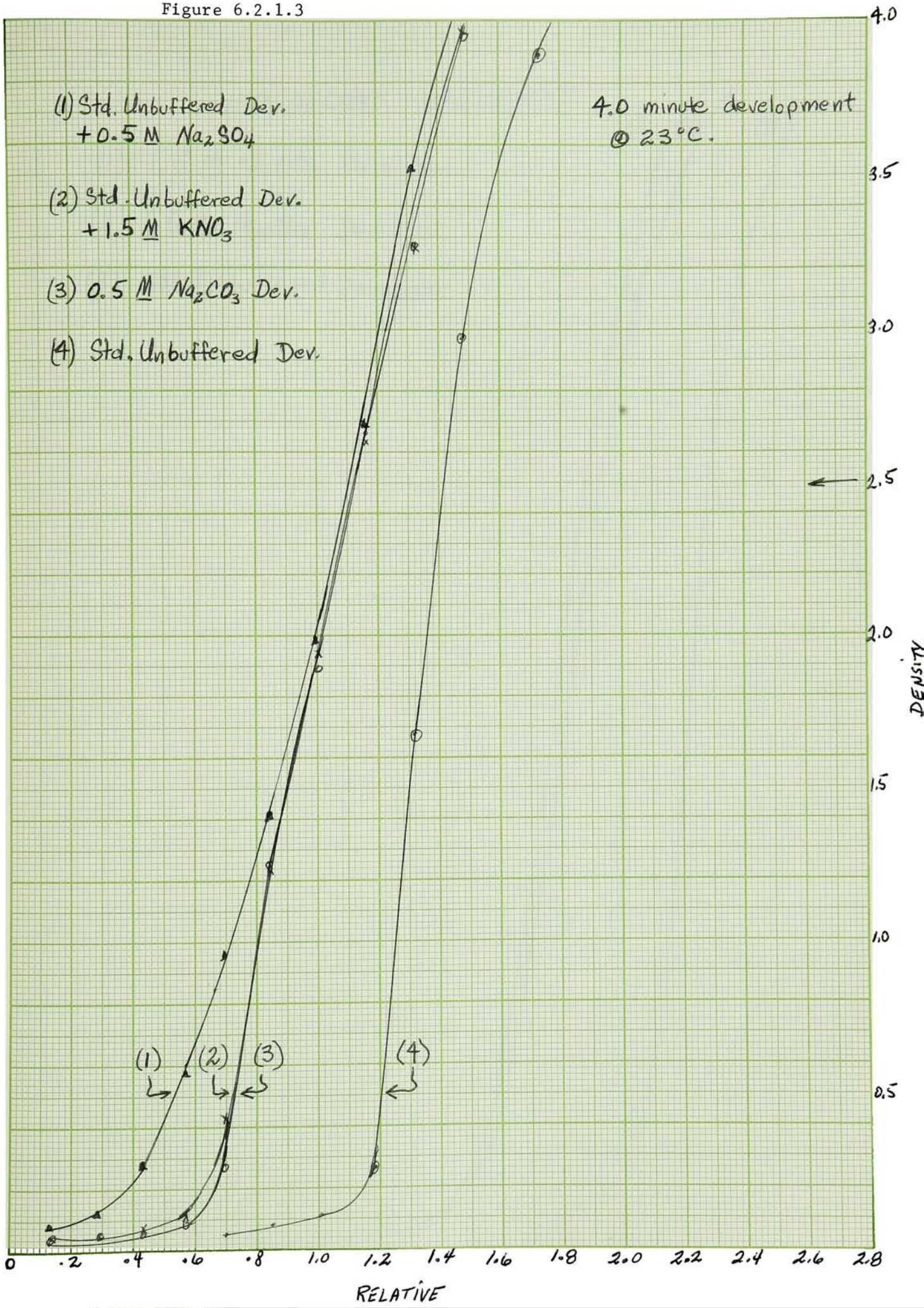

(1) Std. Unbuffered Dev. +0.5 M Na_2SO_4
(2) Std. Unbuffered Dev. +1.5 M KNO_3
(3) 0.5 M Na_2CO_3 Dev.
(4) Std. Unbuffered Dev.
4.0 minute development @ 23°C.
(1)
(2)
(3)
(4)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
DENSITY
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
RELATIVE

Figure 6.2.1.4

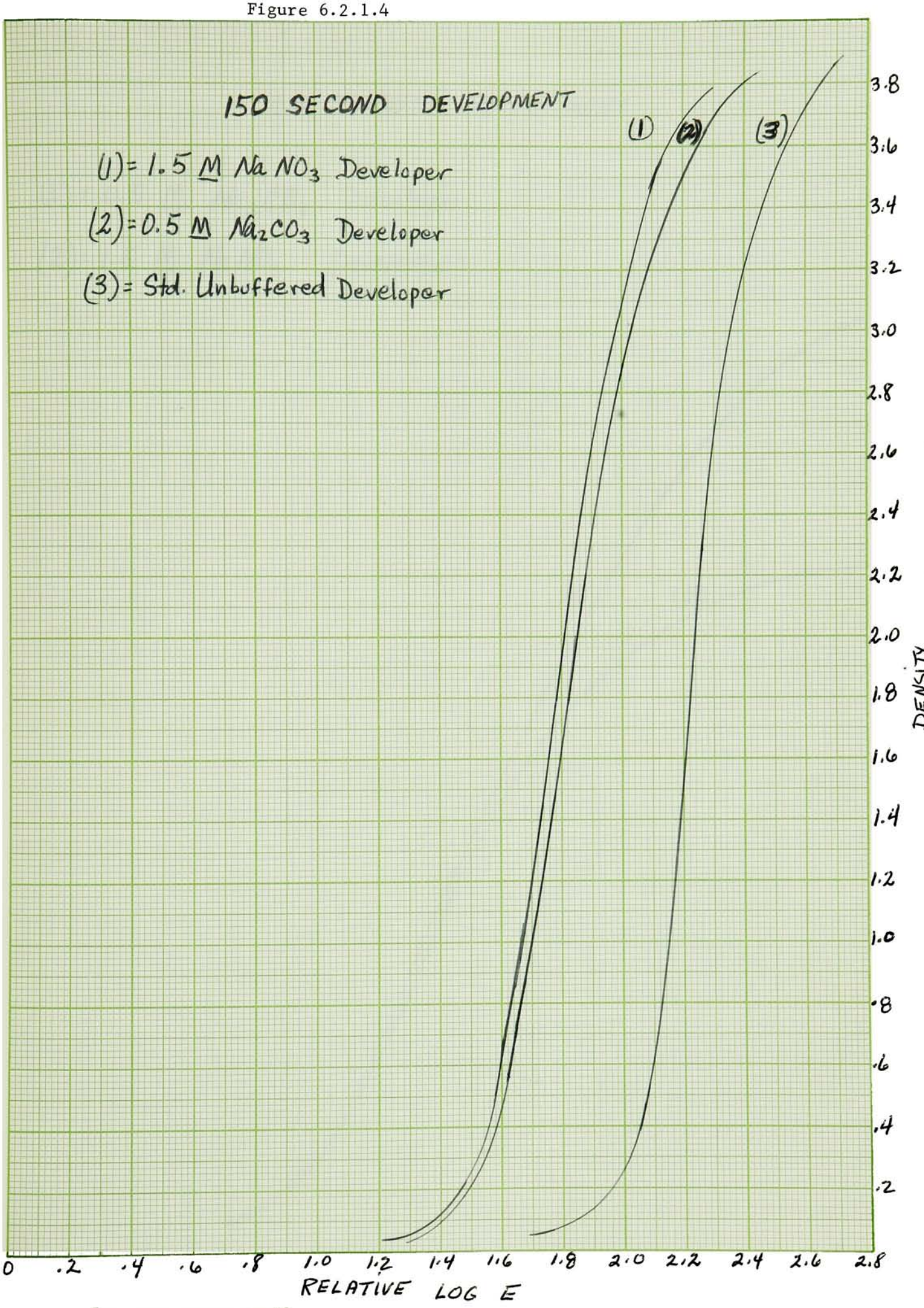
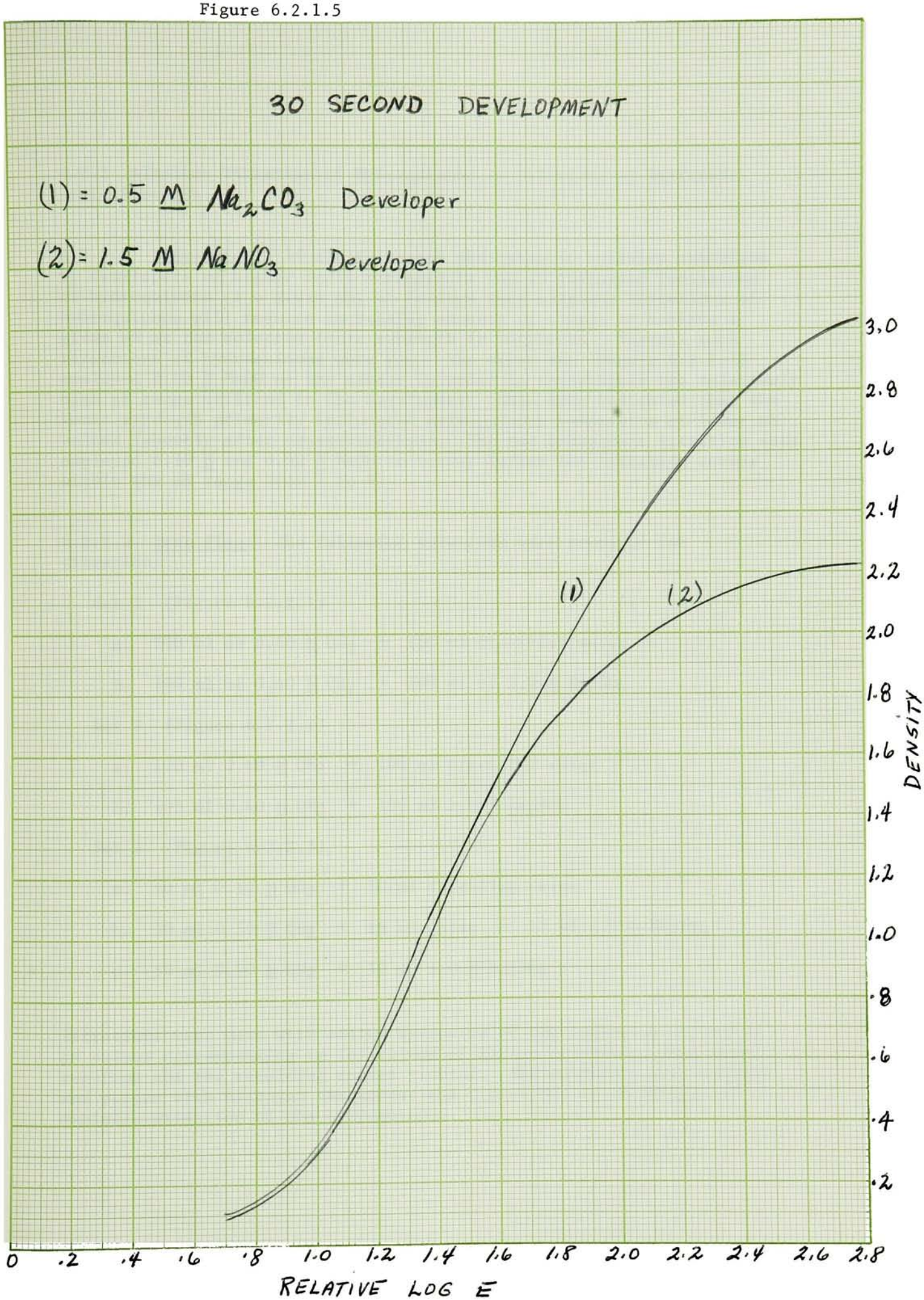

150 SECOND DEVELOPMENT
(1) = 1.5 M $NaNO_3$ Developer
(2) = 0.5 M Na_2CO_3 Developer
(3) = Std. Unbuffered Developer
(1)
(2)
(3)
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
DENSITY
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
RELATIVE LOG E

Figure 6.2.1.5


30 SECOND DEVELOPMENT
(1) = 0.5 M Na_2CO_3 Developer
(2) = 1.5 M $NaNO_3$ Developer
(1)
(2)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
DENSITY
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
RELATIVE LOG E

6.2.2 Alkaline Titration of Hydroquinone in Solutions of Different Ionic Strength

6.2.2.1 Discussion: If the increased photographic activity exhibited by developers of higher ionic strength is due to increased ionization of hydroquinone at a given pH; it follows that alkaline titrations of hydroquinone will require increasing amounts of alkali to achieve a given pH as the solution ionic strength is increased. Several such titrations of hydroquinone were run. The first set (Figure 6.2.2.1) employed 0.60 N NaOH as the alkali in order to investigate the relatively high pH range utilized in the developers. This data indicated that the ionic strength primarily influenced hydroquinone ionization at lower pH values (shortly after neutralization). The two subsequent titration sets employed 0.10 N and 0.20 N NaOH to better define the titration curves within the pH range from 7 to 9.

6.2.2.2 Test Plan: The following solutions were prepared for titration:

Set 1 (Figure 6.2.2.1)

a. 100 ml of 0.40 M QH_2 + 100 ml distilled water

b. 100 ml of 0.40 M QH_2 + 100 ml of 1.0 M Na_2SO_4

Set 2 (Figure 6.2.2.2)

a. 100 ml 0.40 M QH_2 + 100 ml distilled water

b. 100 ml 0.40 M QH_2 + 100 ml 1.0 M Na_2SO_4

Set 3 (Figure 6.2.2.3)

a. 50 ml 0.50 M QH_2 + 50 ml distilled water

b. 50 ml 0.50 M QH_2 + 25 ml water + 25 ml 1.0 M Na_2SO_4

c. 50 ml 0.50 M QH_2 + 50 ml 1.0 M Na_2SO_4

Titrations were made with sodium hydroxide of the indicated normality. pH values corresponding to the volume of sodium hydroxide added were recorded and the resulting curves plotted. The solutions were covered and purged with nitrogen throughout the titrations in an effort to minimize oxidation of the hydroquinone.

6.2.2.3 Test Results: Figures 6.2.2.1, 6.2.2.2 and 6.2.2.3 are plots of pH vs ml of NaOH added for the solutions described above. Table 6.2.2.3 compares the volume of 0.10 N NaOH required to reach the indicated pH value in titration set #2. All of the curves indicate that the maximum difference in alkali required is achieved in the pH range from 8 to 9. We would presume then that the maximum difference in photographic activity would also be exhibited at some point in this pH range. Figure 6.2.2.4 shows the D-Log E curves obtained from two hydroquinone developers at pH 8.80, differing only in solution ionic strength. The aerial duplicating film strips were still-developed in a tray for 30 minutes at 70 degrees F. It is probable that an even larger relative activity difference could be obtained at a lower pH. These results, however, seem sufficient to demonstrate the magnitude of activity differences attributable to increased ionic strength.

TABLE 6.2.2.3

pH	Ml 0.10 N NaOH Required (A) No Salt	(B) Salt Added	(B)(A)	(B-A)
7.5	1.0	1.9	1.9	0.9
8.0	2.5	5.0	2.0	2.5
8.25	4.5	9.0	2.0	4.5
8.50	8.0	16.0	2.0	8.0

6.2.2.4 Conclusion: These tests indicate that:

(1) Hydroquinone ionization is influenced by solution ionic strength.

(2) The effect of increased ionic strength seems to assert itself over the pH range from 7 to about 9. There does not appear to be any additional ionization due to salt effects above a pH of about 9. The difference however is maintained.

(3) Changing solution ionic strength from essentially 0 to 0.75 molar causes a much greater change in hydroquinone ionization that does increasing the ionic strength from 0.75 molar to 1.5 molar. Going from 0.75 molar to 1.5 molar ionic strength does however have a measurable effect on the titration curve (Figure 6.2.2.3) and presumably on hydroquinone ionization and photographic activity.

(4) The concentration of ionized hydroquinone is doubled in the pH range from 8 to 8.5 (Figure 6.2.2.2) by increasing ionic strength from essentially zero to 1.5 molar. At least, twice the amount of alkali is consumed in reaching a given pH and we have to assume that this difference in added alkali is going into increased ionization of hydroquinone.

The hydroquinone ionization constants, K_1 and K_2, were determined spectrophotometrically by Baxendale and Hardy at 20 degrees C and at a constant ionic strength of 0.65 molar. (Reference #9) Our data indicate that higher values for K_1 and K_2 would be derived at even higher solution ionic strength, but we do not know if the difference would be significant.

Increasing ionization of hydroquinone with increasing ionic strength can be rationalized on the basis of the Debye-Huckel theory, with some interesting implications. Reference #10 gives a readily understandable treatment of the influence of ionic strength on reaction rates (and therefore on equilibrium concentrations) based on the Debye-Huckel theory.

The treatment begins with consideration of a reaction between species A and B proceeding through the activated complex AB*, or $A + B \longrightarrow (AB^*) \longrightarrow$ Products. Debye-Huckel equations are applied to this situation and the following form on the Debye-Huckel equation is derived:

$$\text{(Eq 6.2.2.4)}\quad \log K_r = \log K_r^{o} + 1.82 \times 10^{6} \sqrt{\frac{U}{D^3 T^3 \sigma}}\,(2 z_A z_B)$$

where,

K_r = rate constant for reaction
K_r^{o} = rate constant for reaction in infinitely dilute solution
D = dielectric constant of solvent
T = absolute temperature
σ = density
$z_A z_B$ = charge on reacting species
U = ionic strength

This equation predicts that a reaction between two positive or between two negative ions will be accelerated by increases in ionic strength whereas a reaction between a positive and a negative ion will be slowed down. (If the reaction is between a charged ion and a neutral molecule, the equation would predict that the reaction should not be subject to salt effects.) It is emphasized that Equation 6.2.2.4 applies quantitatively only to dilute solutions in which interionic attraction is at a minimum. For more concentrated solutions the equation still predicts the direction in which ionic strength influences reaction rates.

Considering now the ionization of hydroquinone that proceeds in two steps,

$$QH_2 + OH^- \longrightarrow QH^- + H_2O$$

and

$$QH^- + OH^- \longrightarrow Q^= + H_2O$$

The foregoing Debye-Huckel treatment would predict that increasing ionic strength would have no influence on the first ionization step but would favor the formation of the doubly ionized form of hydroquinone. Since our titration data indicate that neutral salts influence hydroquinone ionization primarily in the 7 to 9 pH range (and then more or less maintain the established difference at higher pH values), it is interesting to speculate if the indicated increased ionization results predominately in QH^- or $Q^=$.

This is particularly interesting in that there has historically been disagreement in photographic science literature as to whether QH^- or $Q^=$ is the predominantly active developing agent. It may well be that there is more $Q^=$ present at a given pH in high salt content developers than is normally recognized.

Little attention is given in the literature to the influence of ionic strength on developer activity. Because photographic developers are usually high in ionic strength (1.0 to 2.0 molar) the influence is overlooked and normally of little practical importance. What reference there is to salt effects (reference #11) usually attribute it a "swamping out" of the negative charge on the gelatin thereby permitting a higher concentration of the negatively charged developing agent at the emulsion surface. Most published data on salt effects can, however, be explained on the basis of the Debye-Huckel theory (i.e. - unionized and singly ionized developing agents show little or no salt effects).

Finally, we should note that the Debye-Huckel theory would predict increasing formation of sulfite and formaldehyde with increasing ionic strength when reacting FBS with alkali ($HO\text{-}CH_2SO_3^- + OH^-$). Test results given in Section 4.5 indicate that this is true.

FIGURE 6.2.2.1

AIKALINE TITRATION of HYDROQUINONE

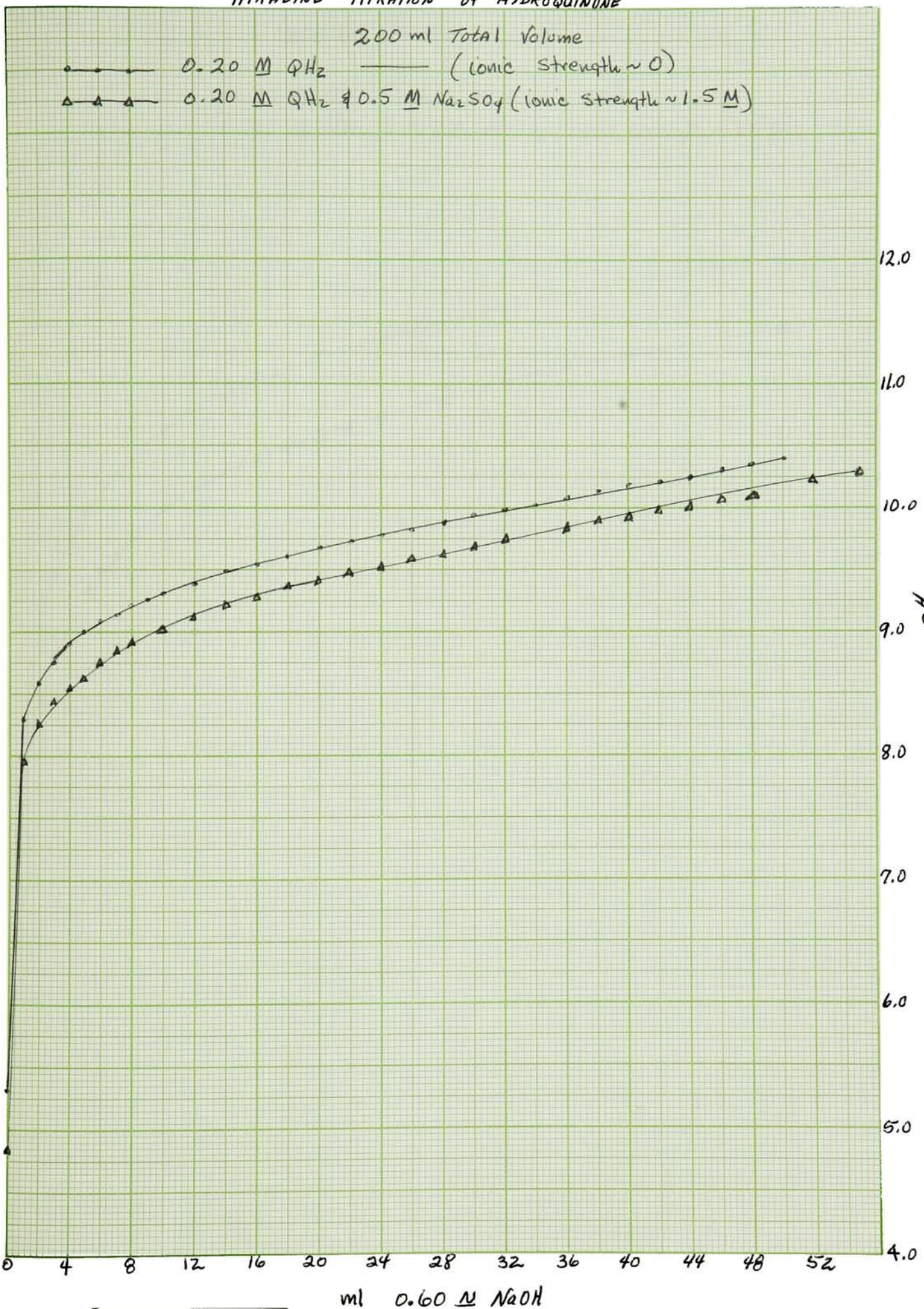


FIGURE 6.2.2.2

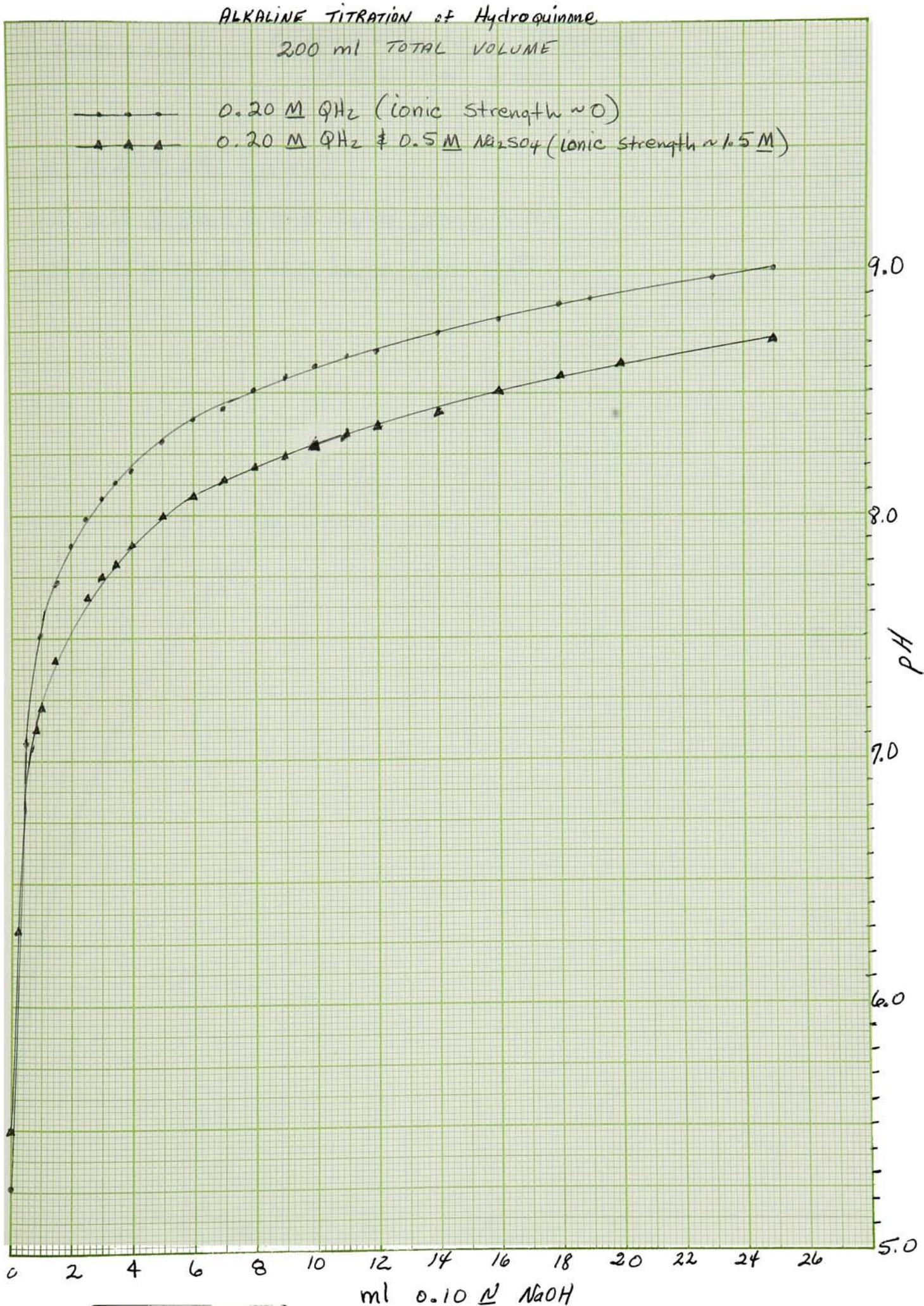

ALKALINE TITRATION of Hydroquinone
200 ml TOTAL VOLUME
0.20 M QH2 (ionic strength ~ 0)
0.20 M QH2 & 0.5 M Na2SO4 (ionic strength ~ 1.5 M)
9.0
8.0
7.0
6.0
5.0
pH
0
2
4
6
8
10
12
14
16
18
20
22
24
26
ml 0.10 N NaOH

FIGURE 6.2.2.3

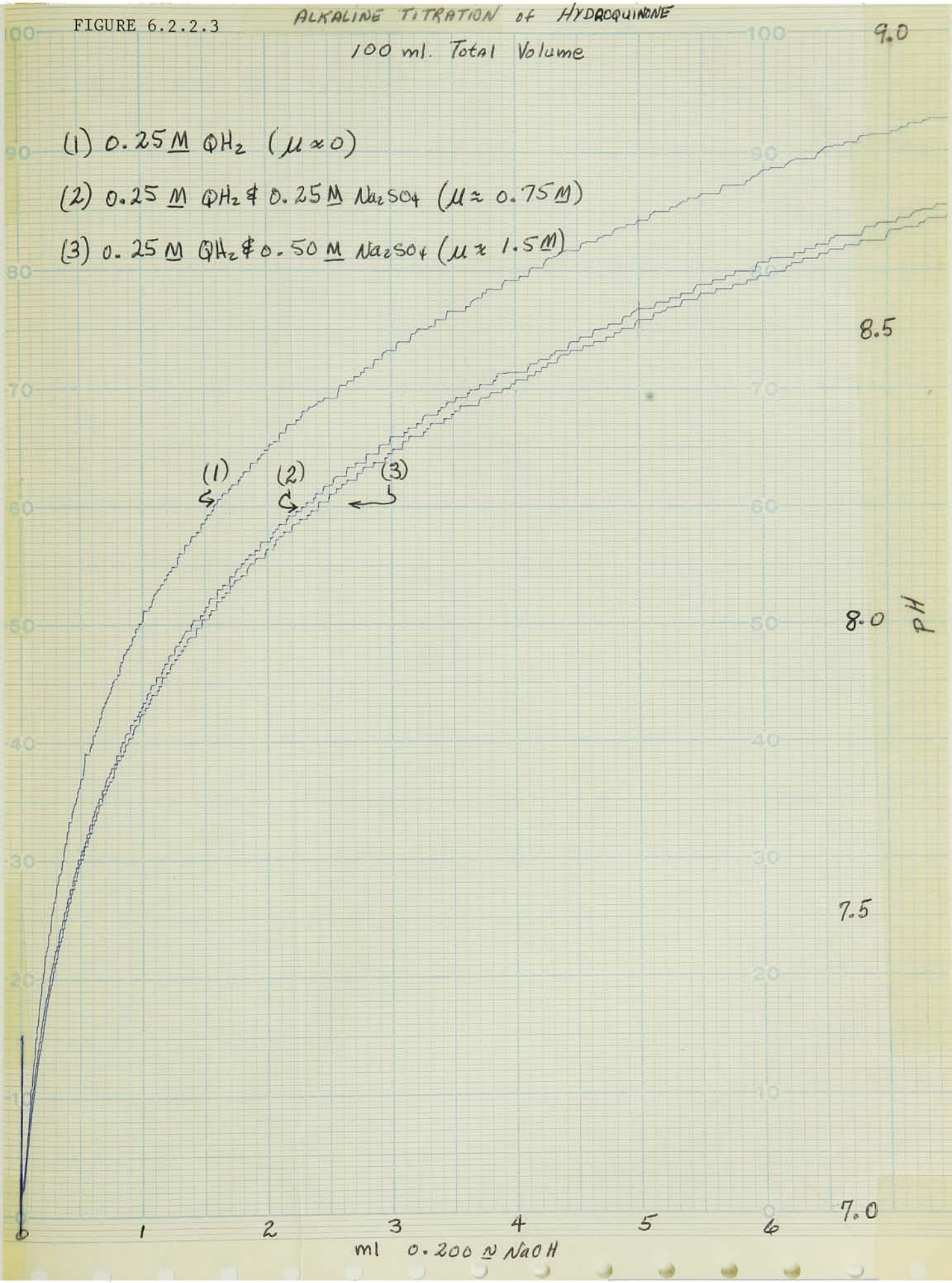
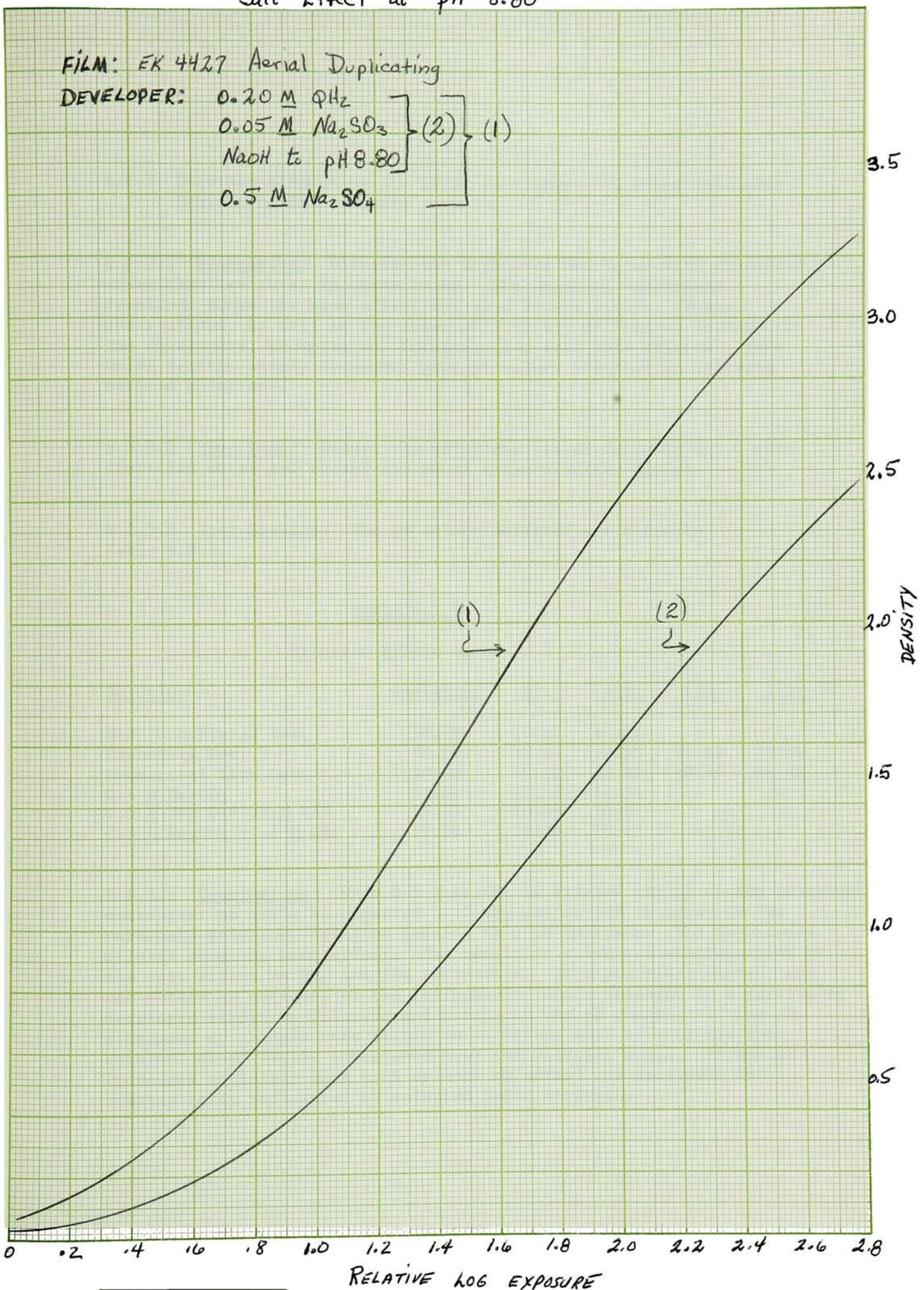

ALKALINE TITRATION of HYDROQUINONE
100 ml. Total Volume
(1) 0.25 M QH2 (μ ≈ 0)
(2) 0.25 M QH2 & 0.25 M Na2SO4 (μ ≈ 0.75 M)
(3) 0.25 M QH2 & 0.50 M Na2SO4 (μ ≈ 1.5 M)
(1)
(2)
(3)
9.0
8.5
8.0
7.5
7.0
pH
0
1
2
3
4
5
6
ml 0.200 N NaOH

FIGURE 6.2.2.4

Salt Effect at pH 8.80



6.2.3 Dilution Effects on the pH of Developers and Other Solutions Exhibiting Salt Effects

6.2.3.1 Discussion: Diluting the Carbonate Developer with distilled water resulted in an increase in pH. The Standard Unbuffered developer shows the same effect but to a lesser extent. These observations, as well as the observed activity difference between the two developers, prompted our investigation into salt effects. This brief section simply documents some pH values obtained on diluting various solutions.

6.2.3.2 Test Plan: Dilute the solutions listed in Table 6.3.4 with distilled water and record the pH at known dilution ratios.

6.2.3.2 Test Results: The pH values obtained are given in Table 6.2.3.

TABLE 6.2.3

Dilution Effect on pH

Solution	Undiluted	1:1	1:3	1:5	1:7
Std. Unbuffered Dev.	10.20	10.22	10.22	-	-
Carbonate Dev.	10.20	10.31	10.39	10.43	10.44
Commercial Lith Dev	10.12	10.22	10.31	10.36	10.38
0.5 M Na_2CO_3	11.44	11.38	11.31	-	-
0.5 M Na_2CO_3 + .5 M FBS	10.52	10.58	10.61	-	-
0.5 M Na_2CO_3 + .1 M QH_2	10.28	10.35	10.45	-	-

6.2.3.3 Conclusions: When 0.5 M Na_2CO_3 is diluted the pH of the solution decreases, as would be expected. If QH_2 and/or FBS is added to the carbonate solution, dilution results in a pH increase. The developers diluted show the same effect. The result is a logical manifestation of the salt effect on QH_2 and FBS ionization. As a practical matter, one can obtain an estimate of the influence of ionic strength in a particular developer simply by dilution and observing the pH change. If the pH decreases or changes very little on dilution, salt effects are non-existent or of little importance over the dilution range. If the pH increases noticably (say 0.05 or more pH units) the developer is substantially influenced by solution ionic strength.

7.0 Major Chemical Changes Occurring When Hydroquinone Developers are Aerially Oxidized

This Section is divided into two parts. The first part deals with chemical analysis of hydroquinone developers containing FBS (lith developers) before and after a measured amount of oxygen is absorbed. The second part similarly deals with hydroquinone developers not containing FBS.

7.1 Aerial Oxidation of Hydroquinone Developers Containing FBS

7.1.1 Discussion: The purpose of these experiments was to determine if we can account for the alkalinity loss in lith developers by determining the quantity of the major oxidation products formed and applying these values to Equations 3.1 and 3.2. These experiments were completed before the alkaline titrations of FBS (Section 4.6) were made. At the time these experiments were run, therefore, we were unaware of the real problem of alkali accountability experienced in reasonably concentrated FBS solutions.

7.1.2 Test Plan: We originally planned to perform replicate oxygen up-take and chemical analyses of the Standard Unbuffered developer and to the same developer with an additional 2.0 grams per liter of Na_2SO_3 added (to better simulate the free sulfite concentration found in lith developers designed for machine processing). Replicate developers with the additional sulfite were run first. When we were preparing the Standard Unbuffered developer for the first run, an error was made in that 6.0 grams of hydroquinone was used in making up the developer instead of 11.0 grams. Once the error was discovered, we decided to complete the run and to replicate using the developer at the lower hydroquinone concentration.

The test plan is to:

(1) Prepare the developer and analyze for QH_2, HQS, Na_2SO_3, HCHO and Na_2SO_4.

(2) Place one liter of the developer in a vaccum desiccator connected to a manometer.

(3) After a period of oxygen absorption, repeat the above analyses plus analysis for NaOH (consumed).

Replicate developers #1 and #2 were prepared as follows:

QH_2	-	0.10 M	
FBS	-	0.50 M	6.0 N NaOH added to yield a pH of 10.20.
Na_2SO_3	-	0.0158 M	
KBr	-	0.017 M	

Replicate developers #3 and #4 were prepared as follows:

QH_2 - 0.055 M
FBS - 0.50 M
KBr - 0.017 M

6.0 N NaOH added to yield a pH of 10.20

7.1.3 Test Results: Analysis results are tabulated in Table 7.1.1. Table 7.1.2 summarizes the results in terms of moles lost or generated.

TABLE 7.1.1

Analysis Results

Developer	QH_2 (g/1)	HQS (g/1)	Na_2SO_4 (g/1)	HCHO (g/1)	Na_2SO_3 (g/1)	Na OH (g/1 consumed)	moles O_2 absorbed	pH
#1 (start)	10.97	0.30	0.22	0.24	3.38	-	-	10.20
#1 (end)	7.44	7.16	3.26	0.98	0.62	0.50	0.0273	10.05
#2 (start)	10.83	0.19	0.29	0.23	3.39	-	-	10.20
#2 (end)	7.17	7.58	3.49	1.01	0.51	0.51	0.0292	10.04
#3 (start)	6.01	0.28	0.50	0.41	2.11	-	-	10.20
#3 (end)	3.42	5.64	3.36	1.12	0.29	0.59	0.0220	9.91
#4 (start)	5.97	0.23	0.38	0.34	2.08	-	-	10.20
#4 (end)	3.30	5.77	3.07	1.10	0.13	0.60	0.0224	9.90

TABLE 7.1.2

Chemical Change in moles

	Developer #1	Developer #2	Developer #3	Developer #4
QH_2 (consumed)	0.0320	0.0332	0.0235	0.0243
HQS (generated)	0.0324	0.0348	0.0253	0.0261
O_2 (absorbed)	0.0273	0.0292	0.0220	0.0224
Na_2SO_4 (generated)	0.0216	0.0224	0.0201	0.0189
NaOH (consumed)	0.0125	0.0128	0.0147	0.0150
HCHO (generated)	0.0246	0.0263	0.0238	0.0253

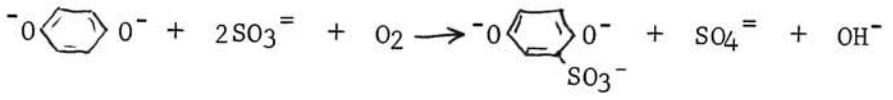
7.1.4 Conclusions: The data indicate that Equation 3.1 (the accepted equation for aerial oxidation of hydroquinone in alkaline solution and in the presence of plenty of sulfite) does not hold for FBS type lith developers. Specifically the data show that:

(1) There is more QH_2 consumed (and HQS formed) than O_2 absorbed.

(2) There is more HQS formed than $SO_4^=$ formed.

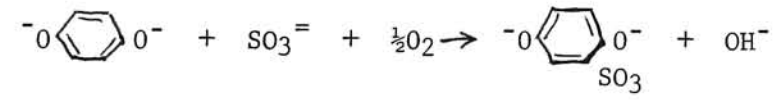
Dr. B. H. Carroll suggested the following treatment of the data in regard to oxygen balance:

Eq 3.1



The equal amounts of $SO_4^=$ and HQS, while verified repeatedly for high sulfite concentrations, do not seem to be a fundamental necessity. There might conceivably be a higher proportion of either one. One can write the equation

Eq 7.1.4



In this reaction only ½ as much O_2 is absorbed as hydroquinone consumed and no sulfate is formed. Looking at the data on the assumption that some of the reaction is by Equation 7.1.4 (and averaging the values for QH_2 consumed and HQS formed as they appear equivalent within the limits of error) we have:

Developer	#1	#2	#3	#4
QH2-HQS Average, mole	0.0322	0.0340	0.0244	0.0252
$SO_4^=$ formed, mole	0.0216	0.0224	0.0201	0.0189
Difference, HQS formed without $SO_4^=$	0.0106	0.0116	0.0043	0.0063
O_2 Required for Reaction 3-1(HQS + $SO_4^=$)	0.0216	0.0224	0.0201	0.0189
O_2 Required for Reaction 7-1-4 (HQS Alone)	0.0053	0.0058	0.0022	0.0032
Total O_2	0.0269	0.0282	0.0223	0.0221
O_2 Consumed, by experiment	0.0273	0.0292	0.0220	0.0224

So if we assume that reaction 7.1.4 can take place, and the excess HQS has been formed by this reaction, we come out with values for oxygen consumed that are in good agreement with the data.

The pH change is greater in developers #3 and #4 than in developers #1 and #2 primarily because of the lower QH_2 concentration used in developers #3 and #4. QH_2 is the primary source of buffer capacity in these developers, therefore, equal alkalinity changes will result in a larger pH change in the developers lowest in QH_2.

The moles of sulfite removed during oxidation can be tabulated as the sum of the moles of HQS and $SO_4^=$ formed. If we assume that no formaldehyde is lost, the treatment used in Section 4.4 is applicable here. Reviewing briefly, we let m = moles $SO_3^=$ removed (equivalent to HQS + $SO_4^=$) and x = moles $SO_3^=$ released by FBS. Then

$$(x) = (HCHO)_{oxidized} - (HCHO)_{initial}$$

$$(m) = (SO_3^=)_{initial} + (x) - (SO_3^=)_{oxidized}$$

The values computed from the data for x and m are:

DEVELOPER	#1	#2	#3	#4
x mole	0.0246	0.0263	0.0238	0.0253
m mole	0.0465	0.0492	0.0382	0.0408
(HQS + $SO_4^=$) mole	0.0538	0.0564	0.0445	0.0441
Ratio m: ($SO_4^=$ + HQS)	0.87	0.87	0.86	0.93

This indicates that some formaldhyde is lost or that the formaldehyde determination is somewhat low. There are indications of the latter in data given in Section 4.3.4 and 4.4.2.

The ratio of $\frac{x}{m}$ is, in theory, that fraction of consumed sulfite that is replaced. The $\frac{x}{m}$ ratios for developers 1 through 4 are 0.53, 0.54, 0.62 and 0.62 respectively. A larger proportion of the removed sulfite is then replaced by disassociation of FBS in developers #3 and #4 thereby justifying, but by no means quantitatively accounting for, the somewhat greater alkalinity loss noted in developers 3 and 4.

If we deal strictly with theory, all of the developers should <u>increase</u> in alkalinity reasoned as follows for developer #1:

0.0322 moles HQS is formed by reaction 3.1 (or 7.1.4) which should result in the formation of 0.0322 moles of OH^-. The amount of FBS disassociating, according to reaction 3.2 and based on formaldehyde analysis, is 0.0246 moles. OH^- should then increase by (0.0322-0.0246) 0.0076 moles. Data in Table 4.6.3, however, indicates that the ratio of OH^- consumed to formaldehyde generated in aqueous FBS solution may be as high as 1.76. If we multiply our 0.0246 moles of formaldehyde formed by this factor and then subtract, we have a probable loss of 0.0112 moles of OH^- compared to a 0.0125 moles found by analysis. The alkalinity loss is then in the range of what we could expect based on <u>all</u> project data. The discrepancy between the values found and that predicted by theory is apparently due to effects documented in Section 4.6.

7.2 Aerial Oxidation of Hydroquinone Developer Not Containing FBS

7.2.1 Discussion: The purpose of this test series is to determine if the deviations from Equation 3.1, noted in the preceding data, are also present in hydroquinone developers not containing FBS.

7.2.2 Test Plan: The aim is to prepare hydroquinone developers with free sulfite concentrations comparable to the FBS containing developers and to have the oxidation take place over a comparable pH range. Chemical analysis is again run before and after a measured oxygen absorption. Nine non-FBS developers were run. All were made up to be 0.10 M QH_2 and 0.017 M KBr. The starting sulfite concentration and pH (again adjusted with 6.0 N NaOH) are as given in Table 7.2.1 for the specific developer. The sulfite concentration was started at high values in the first few samples then decreased to include the concentration range typical of lith developers.

7.2.3 Test Results: Table 7.2.1 gives the starting and ending sodium sulfite concentration and pH values; the moles oxygen (absorbed), QH_2 (consumed), HQS (generated), Na_2SO_3 (consumed), Na_2SO_4 (generated) and NaOH (generated). The value given in Table 7.2.3 for the moles of Na_2SO_4 generated is computed from (moles Na_2SO_3 consumed) - (moles HQS generated). This value is given because we believe it to be more accurate than the EDTA/barium titration of total sulfate, that, in itself, is dependent on the Na_2SO_3 determination. Na_2SO_4 values obtained by each method are compared in Section 8.3. Use of either method does not significantly change the conclusions to be drawn from the data.

TABLE 7.2.3

Developer	pH Range Start-End	Na_2SO_3 (g/l) Start-End	moles O_2 Absorbed	moles QH_2 Consumed	moles HQS Generated	moles Na_2SO_4 Generated	moles Na_2SO_3 Consumed	moles NaOH Generated
A	10.23-11.05	49.80-37.31	0.0120	0.0122	0.0121	0.0127	0.0248	0.0118
B	10.22-11.21	24.76-10.55	0.0143	0.0148	0.0142	0.0140	0.0282	0.0145
C	10.30-11.40	24.80- 8.95	0.0149	0.0154	0.0154	0.0160	0.0314	0.0153
I	9.90-10.19	16.35-10.88	0.0104	0.0106	0.0111	0.0106	0.0217	0.0088
D	9.62-10.50	16.60- 1.71	0.0144	0.0148	0.0146	0.0150	0.0296	0.0127
E	9.64- 9.98	6.20- 0.86	0.0107	0.0121	0.0118	0.0094	0.0212	0.0091
F	9.84-10.20	6.11- 0.05	0.0131	0.0148	0.0148	0.0092	0.0240	0.0097
G	9.84-10.04	3.91- 0.51	0.0102	0.0127	0.0120	0.0083	0.0203	0.0091
H	9.83-10.05	3.83- 0.50	0.0105	0.0126	0.0130	0.0068	0.0198	0.0090

7.2.4 Conclusion: The data indicate that some HQS is being formed without accompanying formation of $SO_4^{=}$ when low sulfite concentrations are used. This is consistent with the results obtained on FBS type developers.

The results are in very good agreement with Equation 3.1 when higher sulfite concentrations are used. It is not clear from the data just where deviation from Equation 3.1 starts to become significant. (The value for the moles of hydroxide generated for developer I would appear to be in error.) Developers E, F, G, and H do show the effect with the magnitude in the latter two being comparable to that found in the FBS type developers.

If we again assume that some of the reaction is by Equation 7.1.4, we have the following oxygen balance for developers E, F, G and H:

Developer	E	F	G	H
QH_2-HQS Average, mole	0.0119	0.0148	0.0123	0.0128
$SO_4^{=}$ formed, mole	0.0094	0.0092	0.0073	0.0068
Difference (HQS formed without $SO_4^{=}$)	0.0025	0.0056	0.0050	0.0060
O_2 Required for Reaction 3.1 (HQS and $SO_4^{=}$)	0.0094	0.0092	0.0073	0.0068
O_2 Required for Reaction 7.1.4 (HQS alone)	0.0012	0.0028	0.0025	0.0030
TOTAL O_2, mole	0.0106	0.0120	0.0098	0.0098
O_2 Consumed by experiment	0.0107	0.0131	0.0102	0.0105

Again we come out with values for oxygen consumed that are in reasonably good agreement with the data. There does, however, appear to be more inconsistencies in this data. I regret that I did not acquire facilities for an independent gravametric $SO_4^{=}$ determination for this test series.

One additional observation can be made on this data that was not possible with the developers containing FBS. That is, at lower sulfite concentrations, the moles of hydroxide generated is less than would be predicted by Equation 3.1. This, also, conflicts with Equation 7.1.4 in that OH^- continues to be ~~found~~ formed in assuming that reaction occurs.

Generally speaking, the data indicate that, as the sulfite concentration is lowered and oxidation proceeds:

(1) HQS continues to be formed essentially quantitatively.

(2) $SO_4^=$ formation is reduced and may not be formed at all at very low sulfite concentrations (compare developers E and F).

(3) OH^- formation (or net increase in solution alkalinity) is reduced and may not be formed at all at very low sulfite concentrations.

(4) The ratio of QH_2 (consumed)/O_2 (absorbed) increases from the 1:1 relationship found at higher sulfite concentrations.

A reaction to fit the data would seem to be one involving QH_2, $SO_3^=$ and O_2 in which no $SO_4^=$ or OH^- is generated. I am unable to derive a satisfactory equation. I must assume, however, that as sulfite is decreased and oxidation proceeds, semiquinone reactions increase in importance. It may be that an answer lies in whether oxygen reacts initially with hydroquinone or with the semiquinone. For example, we can write oxidation equations for the semiquinone in which OH^- is not generated, but peroxide formation, and therefore $SO_4^=$ formation, is predicted. Undoubtedly there are a number of competitive reactions that can be written for the oxygen. This is all highly speculative, however, and best be left to await more data, including kenetic studies.

SUMMARY OF CONCLUSIONS

I. ESTABLISHING AND ACCOUNTING FOR THE ALKALINITY LOSS IN AUTOXIDIZED LITH DEVELOPERS

A. Lith developers lose alkalinity when aerially oxidized.

B. The alkalinity loss is due primarily to the alkaline disassociation of FBS.

C. A much smaller contributing factor to the alkalinity loss in developers containing FBS rests in the finding that the ratio of hydroxide generated to hydroquinone oxidized is less than 1.0 when any developer with sufficiently low sulfite is aeriated.

D. Equilibrium constants, ranging from approximately 3 to 7, were experimentally derived for the alkaline disassociation of FBS. The value of the equilibrium constant increased with increasing solution ionic strength.

E. The overall alkalinity loss cannot be accounted for quantitatively. Alkaline titration of FBS apparently consumes more hydroxide than can be accounted for in the reaction products.

F. Alkaline titration of FBS with corresponding sulfite and formaldehyde analyses showed that 1.4 to 1.8 times as much hydroxide is apparently consumed than sulfite or formaldehyde generated. Alkalinity losses measured in autoxidized lith developers are consistent with these ratios of hydroxide consumed to formaldehyde generated.

G. Our inability to account for the hydroxide apparently consumed is attributed to the possibility of hydroxide ions being present as some intermediate or inactive form, due to interionic attraction, in these relatively concentrated ionic solutions.

II. THE EFFECTS OF AERIAL OXIDATION ON LITH DEVELOPER ACTIVITY

When an FBS type lith developer is aerially oxidized photographic activity is influenced as follows:

A. The free sulfite concentration decreases, resulting in a slight increase in developer activity. A typical decrease in sulfite concentration from 1.8 g/l to 0.7 g/l results in an activity increase in the developer equivalent to 0.05 log E.

B. Hydroquinone is oxidized to hydroquinone monosulfonate resulting in a loss of developer activity.

C. Hydroquinone monosulfonate, thus generated, exhibits measurable developing activity that compensates somewhat for the activity loss due to hydroquinone oxidation. In our samples, activity increases ranging from 0.06 to 0.16 log E is attributable to HQS activity. HQS activity is of particular concern in lith development in that it promotes increased toe speed and decreased contrast.

D. The developer decreases in pH resulting in decreased photographic activity. The developer activity loss attributable to this alkalinity loss is a significant part of the total activity loss due to aerial oxidation.

III. SALT EFFECTS

A. Increasing solution ionic strength increases the activity of hydroquinone developers.

B. The increased activity is attributed to increased ionization of hydroquinone. This contention is supported by data showing that more alkali is required to titrate a hydroquinone solution to a given pH as solution ionic strength is increased.

C. Alkaline titrations of hydroquinone solutions indicate that increasing ionic strength from essentially zero to 1.5 molar can double the amount of ionized hydroquinone at a pH of 8.50.

D. Photographic activity increases, attributable to increased ionic strength, were found to be of a magnitude of about 0.30 log E units in this work.

E. Equivalent results were obtained using either sodium or potassium salts.

F. The developer buffer capacity appears to have no significant influence on lith developer activity until the rate becomes diffusion limited.

G. The influence of solution ionic strength on hydroquinone ionization seems to take place over the pH range from 7 to about 9. There does not appear to be any <u>additional</u> ionization due to salt effects above a pH of about 9.

H. The Debye-Huckel theory predicts that increasing ionic strength would increase the reaction rate between singly ionized hydroquinone and hydroxide ions thereby promoting the formation of doubly ionized hydroquinone. It is conceivable that more doubly ionized hydroquinone exists at lower pH values than is normally recognized.

I. Salt effects on the alkaline reactions of hydroquinone and FBS can be rationalized on the basis of the Debye-Huckel theory, although it is recognized that Debye-Huckel equations apply quantitatively only to dilute solutions. For more concentrated solutions, the equation still predicts the <u>direction</u> in which ionic strength influences reaction rates.

J. Developers exhibiting significant salt effects increase in pH when diluted with distilled water. A quick check of the influence of salt effects in a particular developer can be obtained by simply diluting the developer and observing the pH change.

IV. MAJOR CHEMICAL CHANGES OCCURRING WHEN HYDROQUINONE DEVELOPERS ARE AERIALLY OXIDIZED

A. The data are satisfactorily explained by reaction 3.1 when developers containing plenty of sulfite are aerially oxidized.

B. When the free sulfite concentration is in the range commonly employed in lith developers, the data are no longer adequately explained by reaction 3.1. Specifically:

1. Although HQS continues to be formed essentially quantitatively, $SO_4^=$ formation is reduced and may not be formed at all at very low sulfite concentrations.

2. OH^- formation (or net increase in solution alkalinity) is reduced and may not be formed at all at very low sulfite concentrations.

3. The ratio of QH_2 (consumed) to O_2 (absorbed) increases from the 1:1 relationship found at higher sulfite concentrations.

C. All of the data except alkalinity changes can be accounted for by a combination of reactions 3.1 and 7.1.4.

D. No set of reactions has been derived to fit the data obtained on the net change in solution alkalinity.

8.0 Analytical Procedures

8.1 pH Determinations: All pH determinations were made with a Beckman model G pH meter employing a Corning triple purpose glass electrode and a saturated calomel reference electrode. A borax buffer and a calcium hydroxide-sodium chloride buffer were used in calibrating the meter. Buffer preparation and general operating techniques are those described in the Eastman Kodak publication "Chemical Control Procedures for Black and White Film Processing", (reference #12). The following standards were adhered to in the routine standardization of the meter:

Borax Buffer	9.20
Calcium Hydroxide - Chloride Buffer	11.92 $\pm$ 0.03
Temperature	72 degrees F $\pm$ 1 degree

8.2 Determination of Free Sulfite in FBS Type Developers

8.2.1 Discussion: The amount of free sulfite is determined by pipeting the developer into a standardized, acidified iodine solution. Excess iodine is then titrated with standardized sodium thiosulfate, the amount of free sulfite being determined by difference. Primary standard grade potassium iodate is used as a stable source of iodine that is generated according to the reaction (reference #13).

$$KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$$

$$I = \frac{KIO_3}{6}$$

Sulfite then reacts quantitatively with the iodine:

$$I_2 + SO_3^{=} + H_2O \longrightarrow SO_4^{=} + 2HI$$

The validity of this test for determining free sulfite in the presence of the formaldehyde-bisulfite complex is based on the assumptions that:

[redacted] The reaction of free sulfite with acidified iodine is essentially instantaneous and occurs at a rate several orders of magnitude faster than equilibrium shifts in the formaldehyde-bisulfite complex when the developer solution is made acidic. The oxidation of the formaldehyde-bisulfite compound by acidified iodine is negligible under the conditions of the test.

The following test data and data presented in Section 4.1 support these assumptions. A test was run to determine if free sulfite determinations were influenced by the amount of HCl used in the procedure or by allowing the acidified iodine to stand for ten minutes after addition of the sample but before back titrating excess iodine. The test was run as follows:

(1) A sample of 1.0 M FBS was adjusted to pH 10.33 with 6.0 N NaOH.

(2) Four 10 ml samples were taken and run through the free sulfite procedure with the following amounts of 6.0 N HCl added:

Sample a. 10 ml
b. 20 ml
c. 20 ml
d. 30 ml

(3) Results obtained were:

a. 5.75 g/l Na_2SO_3
b. 5.82 g/l Na_2SO_3
c. 5.75 g/l Na_2SO_3
d. 5.69 g/l Na_2SO_3

(4) After the alkaline FBS solution had stood for about 30 minutes, two 10 ml samples were run. Sample e was titrated immediately while Sample f was allowed to stand in a stoppered flask for 10 minutes before titrating. Results obtained were:

e. 5.48 g/l
f. 5.48 g/l

This test indicates that the amount of HCl used is not critical and that FBS is stable (not subject to oxidation) in acidified iodine.

8.2.3 Reagents: 0.02 N $Na_2S_2O_3$ is prepared by dilution of 0.1000 N $Na_2S_2O_3$ and is standardized daily against 0.1000 N KIO_3. Preparation of all other reagents is outlined in reference 1.

8.2.4 Procedure:

(1) Volumetrically pipet 10 ml of 0.1000 N KIO_3 into a 250 ml erlenmeyer flask. Add about 10 ml of distilled water.

(2) Add 10 ml 0.6 N KI and 15 ml of 6.0 N HCl.

(3) Volumetrically pipet 10 ml of developer into the iodine solution while gently swirling the flask.

(4) Titrate with 0.02 N $Na_2S_2O_3$ to a light yellow color. Add 5 ml of starch indicator solution and continue titration until the blue color just disappears.

$$\text{g/l Free Sulfite (as } Na_2SO_3) = \left((10 \times 0.1000) - (\text{ml } Na_2S_2O_3 \times \underline{N}\ Na_2S_2O_3) \right) \times 6.303$$

8.3 Determination of Sulfite and Sulfate in Non-FBS Developers

8.3.1 Discussion: This analysis procedure is suitable for developers that do not contain the formaldehyde bisulfite complex. It was used in this project on developers A through I in which the total sulfite concentration was in the free state (as Na_2SO_3). The procedure involves the standard iodimetric determination of sulfite in which all sulfite is oxidized to sulfate. Total sulfate is then determined on the same solution employing an EDTA/barium titration.

First the developer is added to an excess of a known quantity of acidified iodine. The excess iodine is then back titrated with standardized thiosulfate enabling the sulfite content to be calculated. The thiosulfate used is oxidized to tetrathionate and does not interfere in the subsequent sulfate determination. Total sulfate, after this oxidation, is measured by addition of excess barium chloride and back titrating the excess barium (not precipitated as $BaSO_4$) with EDTA using methyl thymol blue indicator. The sulfate content is the difference between the total sulfate and the sulfite content converted to equivalent sulfate.

The general validity of this test was determined by running the analysis on a developer sample to which 0, 10 and 20 g/l sodium sulfate was added. The following results were obtained.

Sample	Na_2SO_3 Conc.	Total Na_2SO_4 Conc.	Developer Na_2SO_4 Conc.
Developer Only	9.73 g/l	11.36 g/l	0.37 g/l
Developer + 10 g/l Na_2SO_4	9.69 g/l	21.45 g/l	10.5 g/l
Developer + 20 g/l Na_2SO_4	9.75 g/l	29.69 g/l	18.7 g/l

It appears that we cannot expect accuracy from the sulfate test any better than about $\pm$ 10%, so it serves actually as a sulfate estimation rather than a good quantitative determination. The primary source of error seems to lie in the unsharp EDTA-barium end point.

It should be mentioned that it is not really necessary to directly determine sulfate changes in developers not employing FBS. We determine sulfite and HQS at the beginning and end of oxidation. Lost sulfite not converted to HQS is present as sulfate; therefore, sulfate formation can be determined by difference. We did, however, make the sulfate determination and the following table is a comparison of the change in moles of Na_2SO_4 in developers A through I as determined by this procedure and as computed by difference:

Sulfate Formation as Determined by Titration vs Calculated from Na_2SO_4 and HQS Analysis Data

Developer	Δ moles Na_2SO_4 (X10-4) by EDTA Titration	Δ moles Na_2SO_4 (X10-4) by Na_2SO_3 difference	% Deviation
A	120	127	+6%
B	130	140	+8%
C	152	160	+5%
D	155	150	-3%
E	102	94	-8%
F	103	92	-12%
G	83	73	-12%
H	82	68	-17%
I	98	106	+8%

8.3.2 Reagents

0.250 M $BaCl_2$ - Dissolve 61.08 grams of $BaCl_2 \cdot 2H_2O$ in about 700 ml of distilled water. Dilute to 1 liter.

0.1000 N EDTA - Dissolve 37.225 grams of Disodium Ethylenediaminetetraacetate ($C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$) in about 700 ml of distilled water. Quantitatively dilute to 1 liter in a volumetric flask.

Methyl Thymol Blue Indicator - Dissolve 0.10 gram in 22 ml of 0.01 N NaOH.

Preparation of all other reagents is given in reference #12.

8.3.3 Procedure:

(1) Volumetrically pipet 25 ml of 0.1000 N KIO into a 250 ml erlenmeyer flask.

(2) Add 50 ml of distilled water, 10 ml of 0.6 M KI and 5 ml of 6.0 N HCl.

(3) Volumetrically pipet 10 ml of developer sample to the flask.

(4) Back titrate the excess iodine with 0.1 N $Na_2S_2O_3$ using a starch indicator.

$$g/l\ Na_2SO_3 = ((25X0 \cdot 1000) - (ml\ Na_2S_2O_3\ C\ N)) \times 12.606$$

(5) Volumetrically pipet 10 ml of 0.250 M $BaCl_2$ into the flask. Add 7 drops of methyl thymol blue indicator. Add 6.0 N NaOH until the indicator just changes from yellow to blue.

(6) Add 10 ml of concentrated NH_4OH and titrate with 0.1000 N EDTA. The end point is indicated by a color change from blue to blue-gray.

$$g/l\ Total\ Sulfate\ (as\ Na_2SO_4) = ((10 \times 0.250) - (ml\ EDTA \times 0.1000)) \times 14.205$$

$$g/l\ Na_2SO_4 = g/l\ Total\ Sulfate - (g/l\ Na_2SO_3 \times 1.1268)$$

8.4 Determination of Sulfate in FBS Developers

8.4.1 Discussion: This procedure is an adaptation of the usual gravametric determination of sulfate in which an excess of barium chloride is added to precipitate barium sulfate that is subsequently filtered, washed, ignited and weighed.

The major difficulty in determining the sulfate concentration in photographic developers stems from the fact that sulfite is always present and readily oxidized to sulfate during the analysis. In this procedure, further oxidation of sulfite is avoided by adding an excess of formaldehyde to the developer sample, thereby converting the free sulfite to the relatively stable formaldehyde bisulfite complex. The excess formaldehyde does not seem to interfere with the precipitation except that its volatility and pungent odor prohibit heating the sample before and during the precipitation. Heating and digesting the sample aids in obtaining a coarse, easily filterable precipitate. We did not, however, experience any difficulty in obtaining a precipitate that settled out rapidly and was easily filtered off. A source of error appeared to be our difficulty in fully igniting the precipitate to constant weight. The Selas filter crucibles had to be ignited inside another dish and it was impossible to heat the precipitate to a constant red glow with available lab burners. Results were consistently 1% to 6% high based on the following samples to which known amounts of sulfate were added.

The indicated amount of sodium sulfate was added to each of four 50 ml aliquots of a standard unbuffered lith developer:

Sample #1	None
Sample #2	0.050 g. = 1.0 g/l
Sample #3	0.100 g. = 2.0 g/l
Sample #4	0.300 g. = 6.0 g/l

Each was carried through the gravametric procedure and the following results were obtained:

Sample #1	0.276 g/l
Sample #2	1.279 g/l
Sample #3	2.284 g/l
Sample #4	6.293 g/l

The error becomes larger as the amount of precipitate increases indicating probable coprecipitation. The procedure, however, seems adequate for its purpose in this project.

8.4.2 Reagents:

0.10 M $BaCl_2$ - Dissolve 2.45 grams of $BaCl_2 \cdot 2H_2O$ in distilled water and dilute to 100 ml.

4.0 M HCl - Dilute a 1.0 N. Acculute standard to 250 ml.

8.4.3 Procedure:

(1) Volumetrically pipet 50 ml of developer into a 150 ml beaker.

(2) Add 10 ml of 37% formaldehyde solution and 50 ml of distilled water.

(3) Immerse pH electrodes in the solution and add 4.0 M hydrochloric acid, until a pH of approximately 2.0 is obtained.

(4) Add slowly, with stirring, 5 ml of 0.10 M barium chloride. Allow precipitate to settle at room temperature.

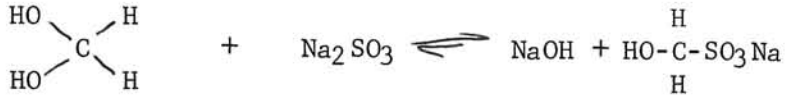
(5) Decant then filter through a tared Selas filter crucible. Quantitatively transfer the precipitate to the crucible and wash thoroughly with distilled water. Check the filtrate for completeness of sulfate precipitation by adding a few drops of $BaCl_2$. No precipitate or cloudiness should appear.

(6) Dry the filter crucible over a low flame, gradually increasing heat until the precipitate attains a dull red glow. Ignite for two hours. Cool in a dessicator and weigh.

g/l Sulfate = wt. $BaSO_4$ X .6105 X 20 (as Na_2SO_4)

8.5 Determination of Free Formaldehyde

8.5.1 Discussion: This procedure is an adaptation of the sulfite method commonly used for assaying formaldehyde solutions. It is based on the following:



A large excess of sodium sulfite is added to a sample of the developer driving the reaction to the right. Essentially all of the formaldehyde is complexed, forming an equivalent amount of sodium hydroxide. The solution is then titrated back to its original pH with 0.10 N acid.

Sodium sulfite has a negligible acid-base buffer effect above a pH of 9.5, therefore, excess Na_2SO_3 does not introduce significant error.

Using: 2.7 as the inverse equilibrium constant for the above reaction, a 50 ml sample of the developer, and adding 1.5 grams of Na_2SO_3, we calculate that on fresh and oxidized developers, approximately 0.03 g/l formaldehyde will not be complexed and, therefore, not accounted for in the titration. That is, results will be low by about 0.03 g/l (or 0.001 molar) based on equilibrium data derived in this project. No attempt is made to correct for this in the computations.

A quick check of the method was made using a reagent grade formaldehyde solution (label assay: 37.4% as HCHO) as a sample. Our analysis equated to an initial HCHO assay of 37.2 %. Additional data on the validity of the test is given in Section 4.3.

8.5.2 Reagents:

(1) 0.1000 N H_2SO_4 - Acculute Standard

(2) Na_2SO_3 Solution - Dissolve 15 grams of reagent grade Na_2SO_3 in distilled water and dilute to 100 ml. Store in a small air-tight bottle. Prepare a fresh solution every 2 or 3 days.

8.5.3 Procedure:

(1) Volumetrically pipet 50 ml of lith developer into a 100 ml beaker. Add a small stirring bar and place on a magnetic stirrer.

(2) Immerse pH electrodes in the solution and carefully determine and record the pH.

(3) Add 10 ml of sodium sulfite solution (1 ml = 0.15 gram) to the solution as it is stirring. The pH will increase due to NaOH formation. Record the new pH.

(4) Titrate with 0.1000 $\underline{N}$ H_2SO_4 back to the original pH. Record the volume of H_2SO_4 required.

g/l Free Formaldehyde = ml H_2SO_4 X $\underline{N}$ H_2SO_4 X 0.060

8.6 Determination of Oxygen Absorbed

The amount of oxygen absorbed by developers in this project was determined by measuring the change in pressure within a vacuum desiccator containing a known volume of developer and a known volume of air. The pressure change from start to end of the oxygen uptake period was determined with an open mercury manometer. Manometer readings were then corrected for any change that occurred in barometric pressure between the start and end of oxygen uptake.

The number of moles of oxygen absorbed can be calculated from the pressure change by using the following general gas law:

$$\Delta PV = n\,RT$$

or

$$n = (\Delta P)\,\frac{V}{RT}$$

where

n = moles of oxygen absorbed
P = pressure change in atmospheres
V = Volume of air space within dessicator in liters
= (total air space - Volume of developer)
R = Gas Constant = 0.082054 liter-atmospheres per degree per mole
T = Temperature in degrees Kelvin

The following is an example of the calculation of oxygen uptake by a typical developer:

Total Air Space = 2.213 liters
Volume of Developer Used: 0.250 liters
V = 2.213 = 0.250 = 1.963 liters
T = 295 degrees K
R = 0.082054 liter-atmospheres/degree/mole

$$p\ (\text{atm}) = \frac{p\ (\text{inches Hg})}{29.921''/\text{atm}}$$

The manometer registered a change of 5.40" while barometric pressure increased by 0.11". The corrected change in pressure is then 5.40 - 0.11 = 5.29" or

$$\Delta p\ (\text{atm})\ \frac{5.29''}{29.921''/\text{atm}} = .1765\ \text{atm}$$

The moles of oxygen absorbed is then:

$$n = \frac{(0.1765)(1.963)}{(295)(0.082054)} = 0.0143\ \text{moles}$$

8.7 Determination of Alkalinity Change (as NaOH)

8.7.1 Discussion: It was necessary to have a method of determining the alkalinity change taking place in a hydroquinone developer undergoing aerial oxidation. We took the approach that this could be done by simply titrating a sample of the developer back to its original pH with standardized acid or base and converting the volume of titrant required to equivalent moles of NaOH generated or consumed during the oxidation period.

After a period of oxidation, the loss in hydroquinone results in the formation of an equivalent amount of hydroquinone monosulfonate. The titration curves for hydroquinone and hydroquinone monosulfonate are not identical and this must be taken into account when attempting to calculate the total change in alkalinity. We attempted to do this by using the titration curves for 0.10 M hydroquinone and 0.10 M hydroquinone monosulfonate attached as Figure 8.7.

8.7.2 Reagents:

0.1000 N H_2SO_4 or 0.1000 N NaOH ------- Acculute Standards

8.7.3 Procedure:

(1) Volumetrically pipet 50 ml of the oxidized developer into a 100 ml beaker. Add a small stirring bar and place on a magnetic stirrer.

(2) Immerse pH electrodes in the solution. Record pH(a) and titrate with 0.10 N acid or base back to the original pH(b). Record the volume of acid or base required.

8.7.4 Correction for Hydroquinone Monosulfonate:

(1) From the attached curves, determine volume of 0.10 N NaOH required to titrate 0.10 M QH_2 from pH(a) to pH(b). Do the same for 0.10 M HQS.

(2) Determine Δ ml by subtracting ml required for 0.10 M HQS from ml required for 0.10 M QH_2 .

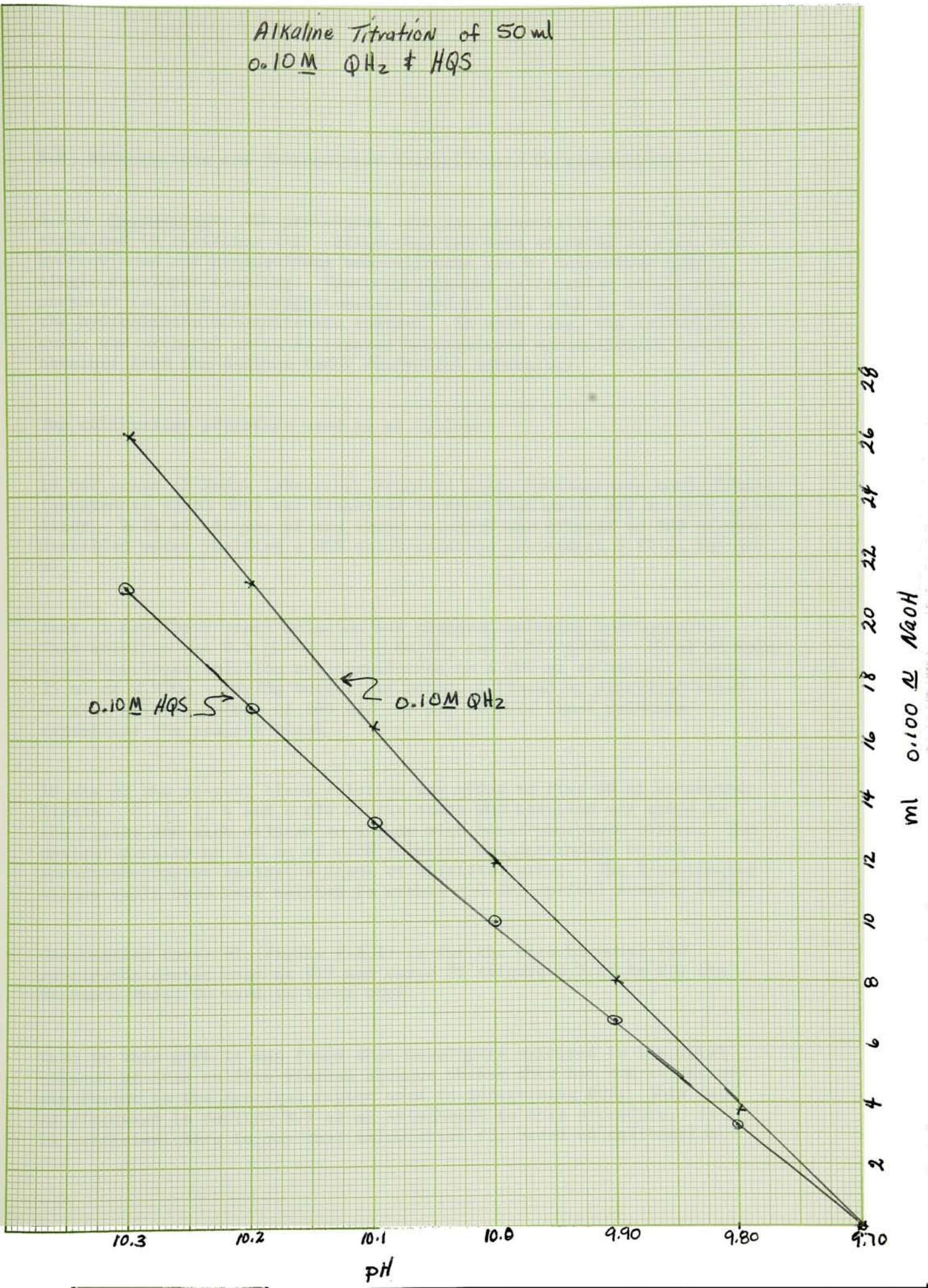
(3) Determine correction by:

$$\text{Titration Correction} = \Delta \text{ml} \times \left(\frac{\text{molar conc. HQS}}{0.10}\right)$$

Calculation of Alkalinity Change:

$$\frac{(\text{ml titrant} + \text{correction}) \times \underline{N} \times 40}{50 \text{ ml}} = \text{g/l NaOH} \begin{matrix} \text{generated} \\ \text{or} \\ \text{consumed} \end{matrix}$$

FIGURE 8.7


Alkaline Titration of 50 ml
0.10 M QH_2 & HQS
0.10 M HQS
0.10 M QH_2
ml 0.100 N NaOH
pH
10.3
10.2
10.1
10.0
9.90
9.80
9.70
2
4
6
8
10
12
14
16
18
20
22
24
26
28

8.8 Hydroquinone and Hydroquinone Monosulfonate Determinations:

8.8.1 Discussion: The procedures used are essentially those given and explained in reference #12. Aliquoting has been adjusted so that both hydroquinone and hydroquinone monosulfonate can be determined from a single developer sampling. Spectrophotometer calibration curves were prepared for both spectrophotometers used in this work in determining the hydroquinone monosulfonate content. In each case, the calibration curve was prepared using an assayed hydroquinone monosulfonate sample obtained from the Eastman Kodak Analytical Laboratory.

The calibration procedure used is as follows:

10.667 grams of Kodak Laboratory Standard grade hydroquinone monosulfonate (assayed at 93.8% HQS) was dissolved in distilled water and diluted to one liter. A 25 ml aliquot of the above solution was diluted to 500 ml with distilled water yielding a HQS stock solution containing 0.50 mg HQS per ml.

Next, a developer stock solution was prepared omitting hydroquinone. This solution was 0.5 M FBS, 0.5 M Na_2CO_3 and 0.017 M KBr. 10 ml of this stock developer solution was transferred to a 100 ml volumetric flask. 35 ml of K_2HPO_4 - KH_2PO_4 buffer was added, followed by distilled water to give a total volume of 100 ml. 10 mls of this final solution represents the reagent blank.

10 mls of the reagent blank solution was added to five 50 ml volumetric flasks. 0, 1, 2, 4 and 6 mls of the stock HQS solution was added to the flasks and each diluted to volume with borax-phosphate buffer. The optical density at 300 mu of each solution was determined on the spectrophotometer against a blank of distilled water. The 1-centimeter silica cells used were matched to within $\pm$ 0.001 optical density units.

Calibration curve #1 (Figure 8.8.1) is for the Hitachi Model 139 spectrophotometer used at RIT and curve #2 (figure 8.8.2) is for the Beckmann Model Du used in later work.

Late in this work it was found that developers oxidized in the total absence of free sulfite yielded aqueous phases that had non-selective absorbance in the spectral region used in determining HQS. This fact is discussed in Section 8.9 as an attachment to this procedure. It is sufficient here to say that calculation #2, based on calibration

curve #2, will correct for this non-selective absorbance while calculation #1, based on calibration curve #1, will not.

8.8.2 Reagents: Preparation procedures for all reagents are given in reference #12.

8.8.3 Procedure:

(1) Extraction and Titration of Hydroquinone

(a) Add 25 ml of K_2HPO_4 - KH_2PO_4 buffer to a 250 ml separatory funnel (I). Volumetrically pipet 5 ml of developer into the funnel.

(b) Add 10 ml of water and 50 ml of water-saturated ethyl acetate and shake for 30 seconds. Allow the phases to separate and carefully transfer the aqueous phase to another 250 ml separatory funnel (II).

(c) Add 50 ml of water-saturated ethyl acetate to funnel II and shake for 30 seconds. Allow the phases to separate and carefully draw off the aqueous phase into a 100 ml volumetric flask, dilute to volume with distilled water and hold for the hydroquinone monosulfonate determination.

(d) Combine the two ethyl acetate phases in funnel I and wash with 10 ml of K_2HPO_4 - KH_2PO_4 buffer, discarding the buffer.

(e) Transfer the combined ethyl acetate phase to a 500 ml beaker. Add 50 ml of methyl alcohol and 50 ml of 7.0 $\underline{N}$ H_2SO_4.

(f) Place on a magnetic stirrer, add 4 drops of Ferroin indicator and titrate with 0.0500 $\underline{N}$ ceric ammonium sulfate.

$$g/l \text{ Hydroquinone} = (0.5505)(\text{ml } Ce^{++++}) - 0.15$$

(2) Determination of Hydroquinone Monosulfonate

(a) Thoroughly mix the 100 ml volumetric flask containing the aqueous phase from part A, step 3.

(b) Volumetrically transfer a 10 ml aliquot to a 50 ml volumetric flask. Dilute to volume with borax-phosphate buffer. Mix thoroughly and transfer a portion of the sample to a clean 1 cm quartz spectrophotometer cell.

(c) Read the sample optical density @ 300 mu vs a blank of distilled water. (Additional readings @260 and 340 mu are required when using Calculation #2)

(Calculation based on calibration curve #1)

g/l hydroquinone monosulfonate = 6.28 (O.D. - 0.044)

(Calculation based on calibration curve #2)

$$\text{g/l hydroquinone monosulfonate} = 6.18 \left(\text{O.D. @ 300 mu} - \left(\frac{\text{O.D. @ 340 mu} + \text{O.D. @ 260 mu}}{2}\right)\right)$$

Figure 8.8.1

#1 — HQS CALIBRATION CURVE @ 300 mμ

Hitachi / Perkin-Elmer Model 139 Spectrophotometer

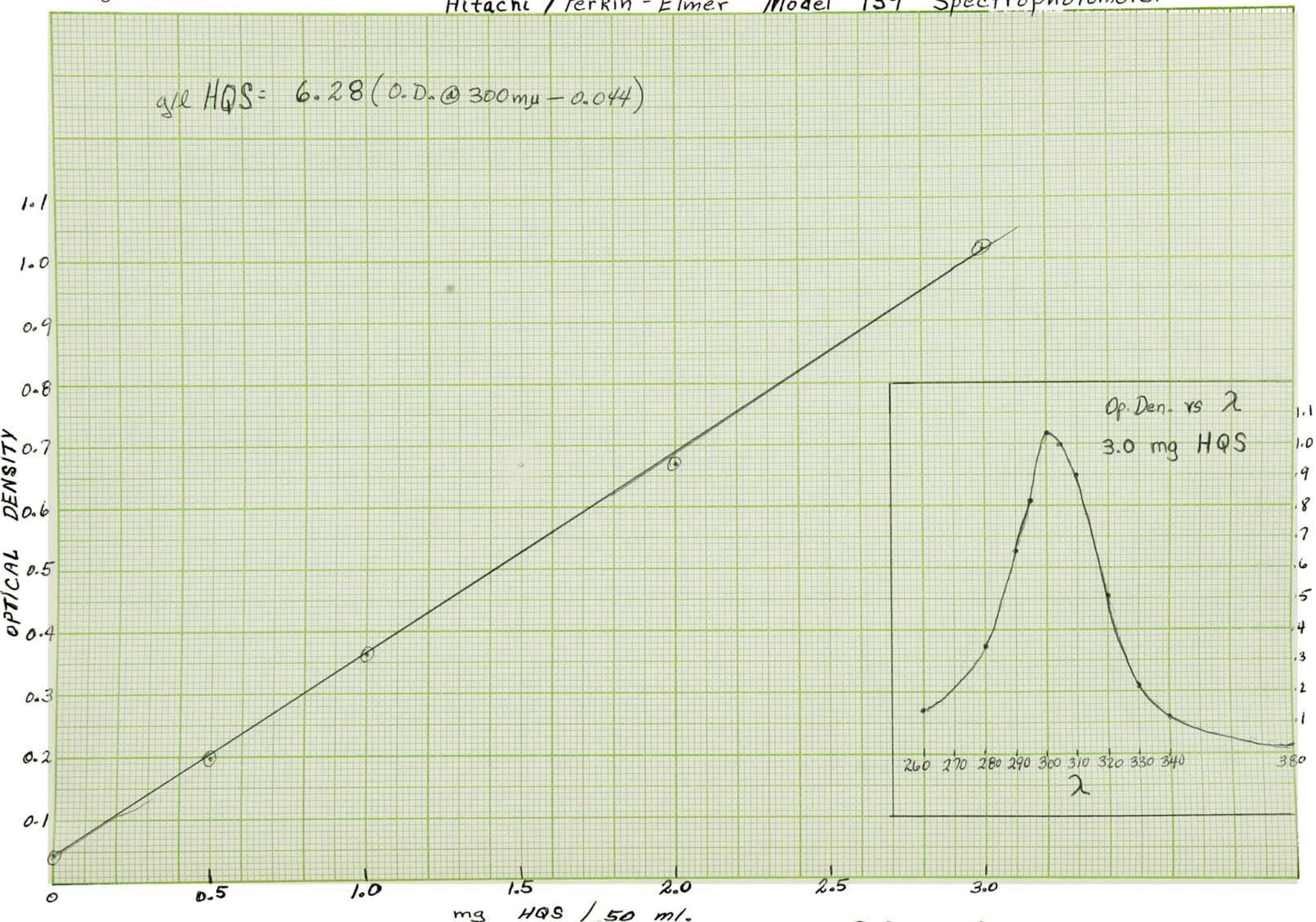


Figure 8.8.2

#2 — HQS CALIBRATION CURVE @ 300 mμ

BECKMAN MODEL DU SPECTROPHOTOMETER

$$\gamma\text{ HQS} = 6.18\left[\text{O.D.@ 300 m}\mu - \left(\frac{\text{O.D.@ 340 m}\mu + \text{O.D.@ 260 m}\mu}{2}\right)\right]$$

OPTICAL DENSITY

1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

0 0.5 1.0 1.5 2.0 2.5 3.0

Op. Den. vs. λ
2.0 mg HQS

0.7
0.6
0.5
0.4
0.3
0.2
0.1

240 250 260 270 280 290 300 310 320 330 340 360

8.9 Influence of Non-Selective Absorbance on HQS Determinations

Late in the lab work, we found that alkaline hydroquinone, oxidized in the absence of sulfite, shows non-selective absorbance at the wavelength (300 mu) used in determining hydroquinone monosulfonate. The implication of this is that absorbance normally attributed to HQS could be due in part to non-selective absorbance of "quinone" type products.

Figure 8.9.1 is a plot of absorbance vs wavelength of alkaline hydroquinone aeriated in total absence of sulfite.

The normal procedure for determining HQS in developers is to use a calibration plot (or its equation) of optical density vs HQS. This is prepared, as described in 8.8, from samples of known HQS concentration. Beer's law is obeyed. A small optical density correction (0.040) is subtracted from the sample optical density corresponding to reagent absorbance (to the intersection of the optical density plot and zero HQS concentration). The assumptions of this technique are:

(1) That HQS is the sole absorbing specie.

(2) That non-selective absorbance is constant at all HQS concentrations.

Figure 8.9.2 shows two spectrophotometric curves. Curve 1 is a developer oxidized to a measured free sodium sulfite concentration of 0.51 g/l. Curve 2 is the same developer aeriated past a point where all free sulfite is expended and part of the hydroquinone oxidation took place in the absence of sulfite.

It is evident from the curves that subtraction of the same non-selective or background optical density (A) from each sample optical density at 300 mu would result in considerable error in calculating the HQS concentration in sample 2. Subtraction of background optical density (B) would yield a more correct value. The revised HQS calculation (calculation #2) given in 8.8 provides for the correction for increased non-selective absorbance. HQS values reported for samples G, H and I (Section 7.2) were calculated by both methods and there was no significant difference in the results, indicating minimal "quinone" formation. We are, therefore, confident that previous HQS values calculated by the standard procedure are not significantly in error and that hydroquinone

is quantitatively converted to HQS in oxidized developers. This is especially true with practical lith developers where the free sulfite concentration rarely goes below 0.50 g/l.

It may well be, however, that measurable "quinone" type products are formed at extremely low sulfite concentrations (0.2 g/l and less). This could probably be determined by careful spectrophotometric analysis using very low sulfite concentrations and controlled oxidation to near zero sulfite concentration. A scanning spectrophotometer would be most useful in such analysis but it could be done by a technique similar to the one given here. In any respect, any future investigation of HQS formation in low sulfite developers should be done in such a way as to guard against additional non-selective absorbance at the wavelength used to measure the sample optical density.

Figure 8.9.1

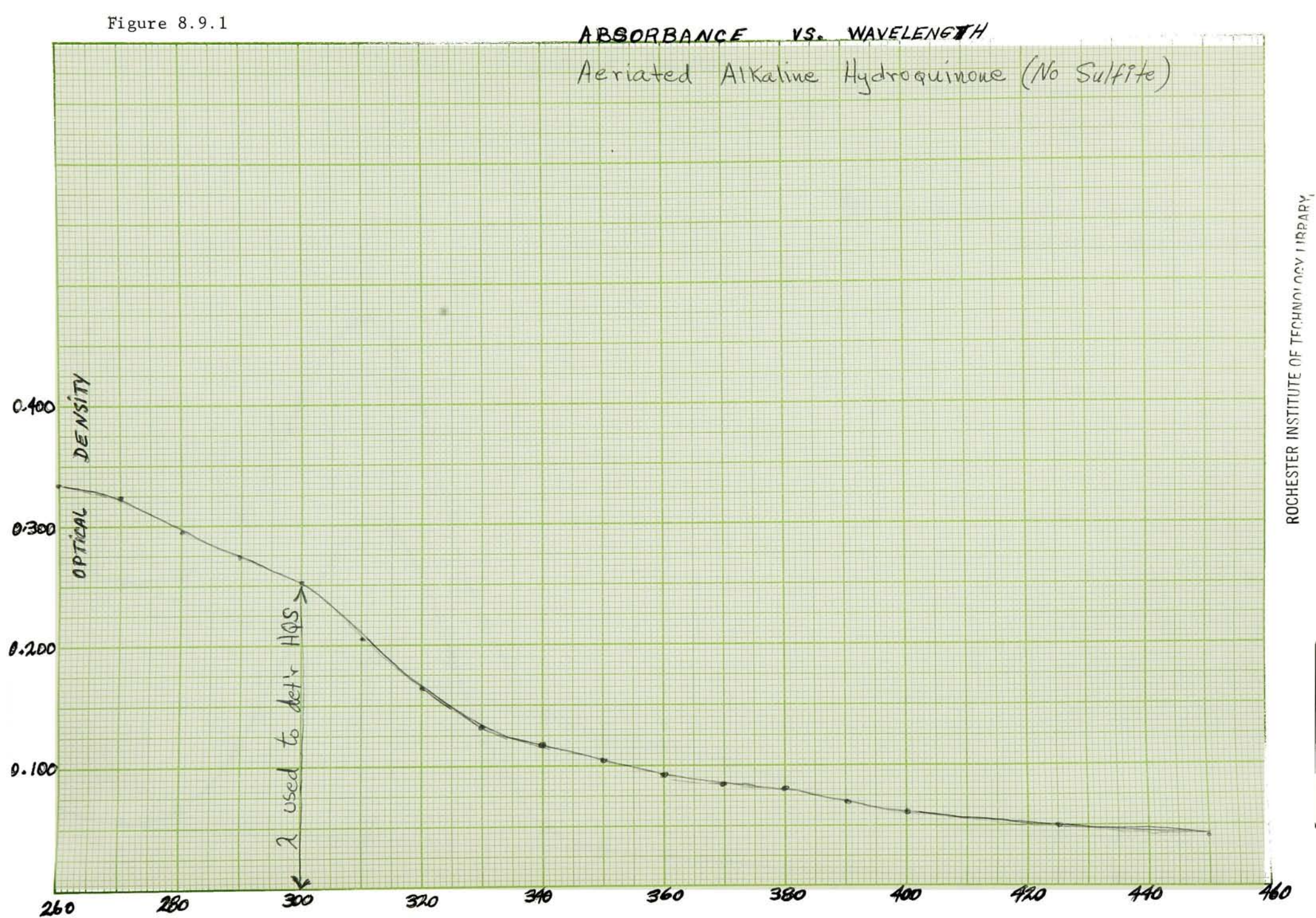
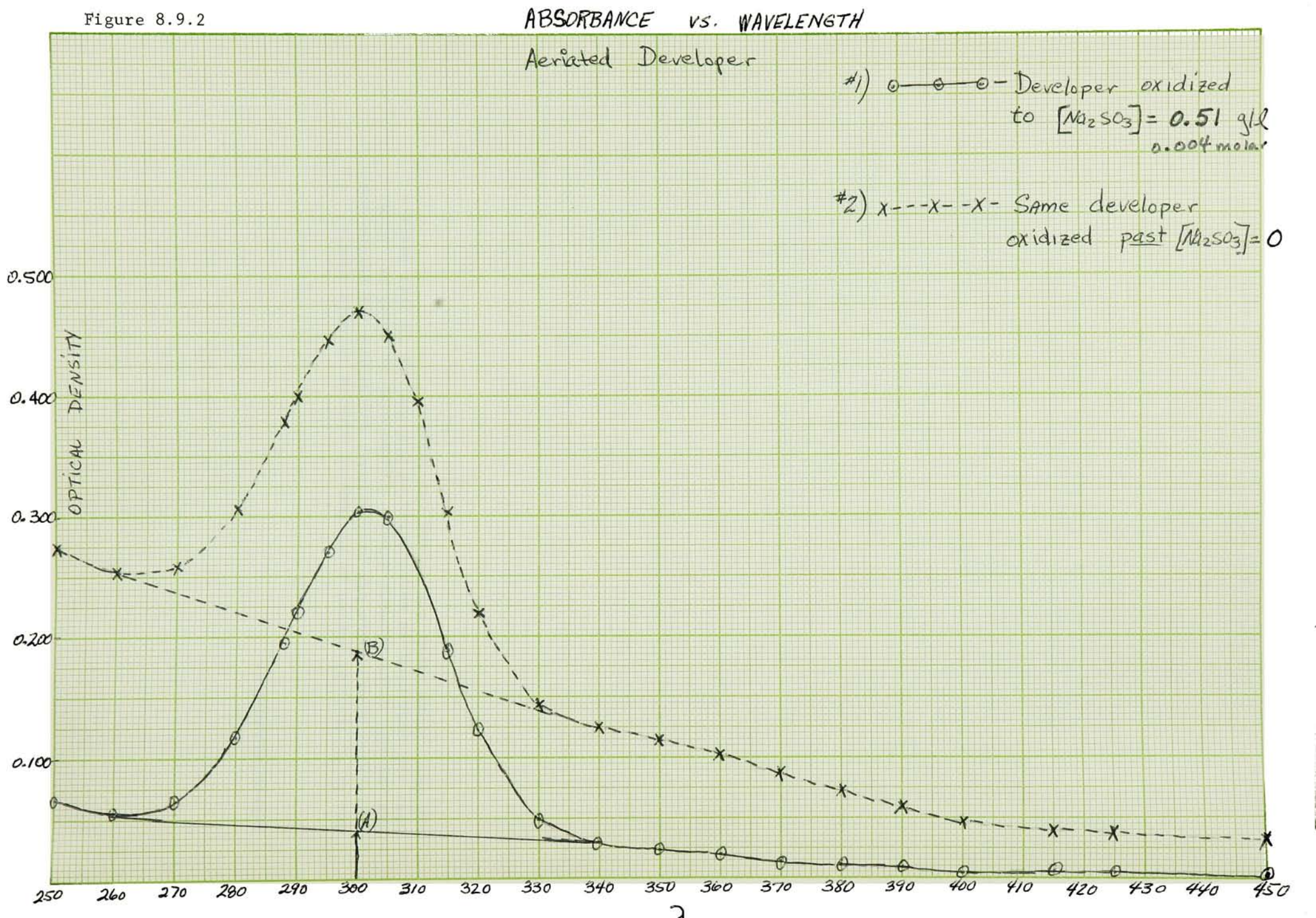


Figure 8.9.2


ABSORBANCE vs. WAVELENGTH
Aerated Developer
#1) Developer oxidized to [Na2SO3] = 0.51 g/l
0.004 molar
#2) Same developer oxidized past [Na2SO3] = 0
OPTICAL DENSITY
0.500
0.400
0.300
0.200
0.100
(A)
(B)
250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

Acknowledgements:

Dr. B. H. Carroll served as my faculty advisor on this thesis. I gratefully acknowledge his professional assistance and advice and the patient encouragement given. I also wish to thank Mr. T. H. Hill for obtaining an assayed lot of HQS for use in this project and Mrs. Linda Jones for typing the thesis.

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